JCF Würzburg

ChemSyStM

Chemie-Symposium der Studierenden Mainfrankens

2018

DIE PERFEKTE MISCHUNG

Abstractband

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Dieser Abstractband besitzt keine Seitenzahlen. Dafür sind jeweils am Rand die Posternummern eingetragen. In eben dieser Reihenfolge sind die Poster auch während der Posterpräsentation aufgestellt. Weitere Informationen können aus den Lageplänen entnommen werden.

Grußwort JCF

Liebe Teilnehmer der Chem-SyStM 2018, sehr geehrte Gäste,

das JungChemikerForum Würzburg freut sich in diesem Jahr zum siebten Mal die ChemSyStM ausrichten zu können. Nach den Erfolgen der vergangenen Jahre sind wir der festen Überzeugung, dass dieser Tag eine ganz besondere Atmosphäre aus Information, Wissenschaft, und Kommunikation bietet. Er bietet quasi „Die perfekte Mischung“. Deshalb haben wir uns in diesem Jahr genau für dieses Motto entschieden.

Aber hier hört die Bedeutung dieses Mottos nicht auf. In der heutigen Zeit braucht es immer mehr perfekte Mischungen, um verschiedenste Herausforderungen effektiv angehen zu können. Nur wenn sich das Wissen und die Erfahrungen verschiedener Wissenschaftler vermischen, können neue Ideen entstehen und alte Fragen beantwortet werden.

Wie in den letzten Jahren bieten wir auch dieses Jahr ein abwechslungsreiches Programm an. Dazu konnten wir Herrn Christian Lange vom VAA (Verband angestellter Akademiker und leitender Angestellter der Chemischen Industrie e.V) gewinnen, um die jungen Chemiker über eine eventuelle Zukunft in der chemischen Industrie zu informieren. Zudem erfolgt ein kleiner Einblick in die Gesellschaft Deutscher Chemiker in einem Kurzvortrag von Herrn Karger. Wie bei jeder ChemSyStM beginnt das wissenschaftliche Programm mit einigen Posterappetizern, die dann nahtlos in die eigentliche Postersession übergehen.

Den Höhepunkt der Veranstaltung stellt der Abendvortrag „Verbinden ohne chemische Bindung“ von Herrn Prof. Rainer Adelung (CAU Kiel) dar. Daran anschließend laden wir alle Anwesenden zu einem gemütlichen Ausklang des ereignisreichen Tages ein, welches eventuell dem ein oder anderen ein zukünftiges Engagement im JungChemikerForum schmackhaft macht.

Wir wünschen Ihnen viel Freude, gute Unterhaltung und einen interessanten Austausch bei der ChemSyStM 2018.

Euer Sprecher-Team des JCF Würzburg

S Endres

Sebastian Endres

Domenik Schleier

Florian Geyer

Florian Geyer

Für eine bessere Lesbarkeit und um einer gleichberechtigten pluralistischen Gesellschaft näher zu kommen, wird im folgenden Text ausschließlich der weibliche Plural verwendet!

Liebe Studierende,

Das Motto der diesjährigen ChemSyStM lautet „Die perfekte Mischung“ und tatsächlich spiegelt das Programm der ChemSyStM die ganze Bandbreite der Forschung in der Fakultät für Chemie und Pharmazie perfekt wieder. Denkt man an Chemie und perfekte Mischung, so denken viele zunächst an die Mischung im Reagenzglas oder Kolben. Damit eine erfolgreiche Synthese gelingt, müssen die reagierenden Stoffe in der richtigen Mischung vorhanden sein. Darüber hinaus muss aber auch das Lösungsmittel perfekt abgestimmt sein. Viele von Ihnen können bestimmt ein Lied davon singen, wie mühsam es ist, die Ausbeuten durch immer neue Mischungsvarianten hochzutreiben.

Das Prinzip der perfekten Mischung gilt aber auch im übergeordneten Sinne für die Forschung, da eine erfolgreiche Forschung selten im stillen Kämmerlein gelingt, sondern für den Erfolg häufig viele sehr unterschiedliche Expertisen benötigt werden. Damit aber eine solche Kooperation gelingt, ist es zunächst erforderlich, dass sich die verschiedenen Komponenten dieser Mischung aus Personen auch untereinander verstehen. Hiermit meine ich nicht ein Verständnis auf einer menschlichen Ebene, obwohl es von enormem Vorteil ist, wenn auch die Charaktere der beteiligten Personen eine für alle verträgliche Mischung darstellt. Was ich meine, ist das fachliche Verständnis. Das ist nicht immer gegeben, da die notwendigen Expertisen selbst in einem Fachgebiet zum einen immer spezieller werden und weil zum anderen häufig sehr unterschiedliche Fachgebiete kooperieren müssen, um einem neuen Naturgeheimnis auf die Spur zu kommen. Daher muss auch die Lehre eine perfekte Mischung aus vielen, häufig sehr unterschiedlichen Zutaten sein, um die Studentinnen fit für das Leben nach der Universitätsausbildung zu machen. Vielleicht benötigt man später mal gerade das, was man im Studium als vollständig unnötig angesehen hat. Sie sehen, perfekte Mischungen wohin man blickt.

Ich freue mich auf interessante Forschungsarbeiten von Studierenden für Studierende und wünsche allen Teilnehmerinnen und Teilnehmern einen spannenden und erkenntnisreichen Tag. Und dabei können Sie direkt das wichtigste Üben für die perfekte Kooperation: Eine auf Verständnis ausgerichtete Kommunikation mit anderen.

Prof. Dr. Bernd Engels
GDCh Ortsverbandsvorsitzender
OV Unterfranken

Grußwort Fakultätsleitung

Sehr geehrte Teilnehmer/innen und Gäste der ChemSyStM,

liebe Mitglieder des JungChemikerForums,

seit nunmehr über 10 Jahren findet im regelmäßigen Turnus das Chemie-Symposium der Studierenden Mainfrankens, kurz ChemSyStM, statt und hat sich somit als fester Bestandteil im wissenschaftlichen Angebot unserer Fakultät etabliert. In einem familiären Rahmen haben Studierende sämtlicher Studiengänge und Promovierende aller Institute, Lehrstühle und Arbeitsgruppen die Möglichkeit, ihre Forschungsergebnisse der Fakultätsöffentlichkeit zu präsentieren und konstruktiv zu diskutieren.

Das diesjährige Motto – „Die perfekte Mischung“ – deutet es bereits an: Die Bandbreite an unterschiedlichen Forschungsschwerpunkten an unserer Fakultät ist groß und vielfältig und die verschiedenen Disziplinen ergänzen sich hervorragend. Dies spiegelt sich in zahlreichen Kooperationsvorhaben zwischen den einzelnen Arbeitsgruppen und Verbundprojekten wider. Die ChemSyStM bietet Ihnen die Möglichkeit, sich über die vielfältigen Forschungsaktivitäten an unserer Fakultät zu informieren. Riskieren Sie einen Blick über den Tellerrand und erleben Sie, wie in Würzburg z.B. Grundlagenforschung und materialwissenschaftliche Anwendungen, präparative und spektroskopische Methoden oder Medizinische und Theoretische Chemie Hand in Hand gehen.

Allen Teilnehmern wünsche ich einen spannenden und inspirierenden Tag. Mein Dank gebührt an dieser Stelle sämtlichen Vortragenden, Sponsoren und natürlich den Mitgliedern des JungChemikerForums, die durch ihr großes Engagement immer wieder aufs Neue das Gelingen der ChemSyStM ermöglichen.

Herzlichst

Ihr

Maik Finze

(Prodekan der Fakultät für Chemie und Pharmazie)

Unterstützer

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Appetizer

#	**Name**	**Vorname**	**AK**	**Kategorie**
4	Ramler	Jacqueline	Lichtenberg	Anorganische Chemie und Materialwissenschaften
13	Scheuring	Nikolai	Lehmann	Organische Chemie und Biochemie
17	Löblein	Jochen	Luxenhofer	Anorganische Chemie und Materialwissenschaften
18	Lübtow	Michael	Luxenhofer	Anorganische Chemie und Materialwissenschaften
39	Huettner	Nick	Luxenhofer	Anorganische Chemie und Materialwissenschaften
48	Singh	Anurag	Röhr	Physkalische und Theoretische Chemie
49	Schäfer	Thomas	Müller-Buschbaum	Anorganische Chemie und Materialwissenschaften
50	Leonhard	Viktoria	Beuerle	Organische Chemie und Biochemie
51	Rupp	Mira	Kurth	Anorganische Chemie und Materialwissenschaften
61	Dembski	Sofia	Dembski	Anorganische Chemie und Materialwissenschaften
69	Haider	Malik Salman	Luxenhofer	Anorganische Chemie und Materialwissenschaften

ABSTRACTS

Bowl-Shaped Polycyclic Aromatic Dicarboximides Containing Various Imide Substituents

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In recent years synthetic approaches have been developed for non-planar polycyclic aromatic hydrocarbons (PAHs) to allow their application in materials science and supramolecular chemistry[1] Being commercially available, bowl-shaped PAH corannulene is the most common precursor to prepare larger or functionalized bowl-shaped molecules. However it is still challenging to enlarge the corannulene scaffold with electron deficient moieties.

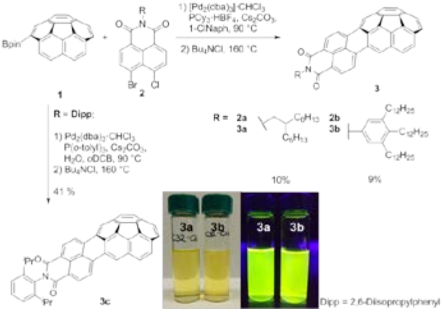

Figure 1. Synthetic strategies towards bowl-shaped PADIs **3a** - **3c**.[4]

We have recently developed a generalized synthetic route to polycyclic aromatic dicarboximides (PADIs) by a palladium-catalyzed Suzuki-Miyaura cross coupling and direct annulation reaction between arylboronic esters and halogenated naphthalene- or perylene- dicarboximides.[2,3] Furthermore, this synthetic strategy could be applied to the synthesis of bowl-shaped PADIs.[4] Here we report the attachment of naphthalene subunits decorated with a variety of imide substituents onto the corannulene core.

[1] H. Ito, K. Ozaki, K. Itami, *Angew. Chem. Int. Ed.* **2017**, *56*, 11144.
[2] S. Seifert, K. Shoyama, D. Schmidt, F. Würthner, *Angew. Chem. Int. Ed.* **2016**, *55*, 6390.
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Light-induced water oxidation with supramolecular ruthenium macrocycles

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Our interest in water splitting as a modern technology for the generation of sustainable energy has motivated us to focus our efforts on the development of supramolecular catalysts for light-driven water oxidation.[1] Recently, we presented our **MC3** catalyst which gathers three Ru(bda) units in a macrocyclic fashion.[2] Molecular dynamics simulations suggest a hydrogen-bonded water network within the catalyst's cavity to be the reason for its very high catalytic activities.[3] Here we introduce electronically and sterically tuned **MC3** derivatives which have been investigated for their application in light-induced water oxidation. The conformational energy landscapes of **MC3** derivatives with *meta*- or *para*-substituted spacer ligands have been evaluated based on metadynamics simulations and the largest experimentally observed activity differences could be assigned to individual steric features.

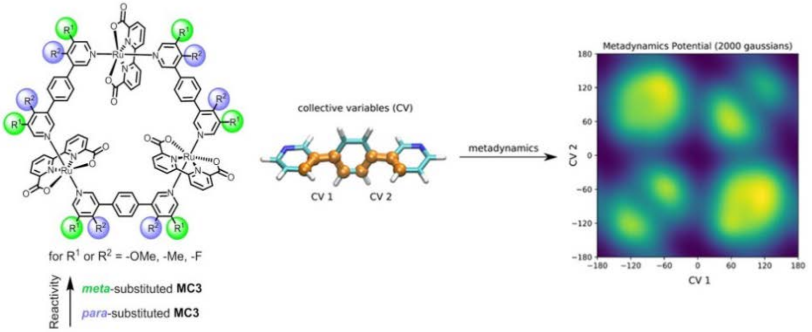

Figure 1. Substituted **MC3** derivatives and study of their conformations using metadynamics simulations.

[1] V. Kunz, D. Schmidt, M. I. S. Röhr, R. Mitrić, F. Würthner, *Adv. Energy Mat.* **2017**, *7*, 1602939.
[2] M. Schulze, V. Kunz, P. Frischmann, F. Würthner, *Nat. Chem.* **2016**, *8*, 576-583.
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Surface modification of detonation nano-diamonds with ozone

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The purification of detonation nano-diamonds (DND) from detonation soot and the removal of non-diamond carbon and graphite is mostly done with strong liquid oxidizers at elevated temperature and pressure. The purification in liquid-phase is both hazardous and costly, making up to 40% of the product cost.[1] The environmentally friendly technology of DND purification using ozonized air at elevated temperatures to oxidize non-diamond carbon and, therefore, eliminating the need in using corrosive liquid oxidizers was first introduced in 1991.[1,2]

There were several efforts to purify DND by oxidation of detonation soot and DND powder with air or oxygen at elevated temperatures. The methods allowed to significantly decrease content of non-diamond carbon and obtain DND with improved dispersibility in solvents.[3]

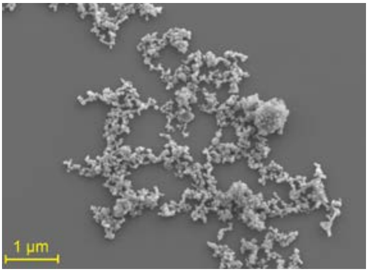

Figure 1. SEM image of diamond nano-particles on a silicon wafer.

One aspect of our research is to further simplify the purification of DND. This is done by reducing the necessary temperature and pressure during the purification. Another important part is the modification of moieties present on the surface. During the treatment with ozone sp^2 carbon reacts with Ozone to form intermediates that can be used to create a large amount of similar moieties on the surface of the DND. This is achieved by the use of oxidizing and reducing agents after the ozonolysis. This process can be performed in liquid-phase and also directly in ozonized air without any solvents, allowing the use of diverse reagents and conditions.

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Bismut-Übergangsmetallkomplexe in der katalytischen Cyclo-Isomerisierung

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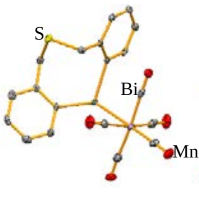
Bismutsalze, BiX_3, werden als Lewis-Säure-Katalysatoren in organischen Transformationen wie z. B. Friedel-Crafts- oder Mannich-Reaktionen eingesetzt (X = Cl, Br, I, O_3SCF_3).[1] Kürzlich konnten wir erstmals eine katalytische Aktivität von Bismutkomplexen mit Bi−ÜM-Bindung beobachten, die auf der Bildung von Radikalspezies beruht (ÜM = Übergangsmetall).[2]

Als Modellreaktion wurde die Cyclo-Isomerisierung von einfachen Iodolefinen gewählt (siehe oben). Für die Stammverbindung, 6-Iod-1-Hexen, konnten katalysierte radikalische Cyclo-Isomerisierungen bislang lediglich unter photochemischen Bedingungen realisiert werden.[3] Mit den neuen Bismutspezies als Katalysatoren gelingt die radikalische Cyclo-Isomerisierung von Iodalkenen wie 6-Iod-1-Hexen erstmals unter thermischen Bedingungen. Testreaktionen zeigten eine wichtige Rolle der Bismutkomponente in den Reaktionen.[2]

Im Rahmen dieser Studien wurden die Bismutkomplexe **1**–**3** synthetisiert, die über eine Bi−Mn, Bi−Fe, bzw. Bi−Co-Bindung verfügen. Um die Polarität der Bi–ÜM-Bindung einschätzen zu können, wurden IR-spektroskopische Messungen sowie Reaktivitätsstudien durchgeführt, beispielsweise mit Diphenyldichalkogeniden.[2]



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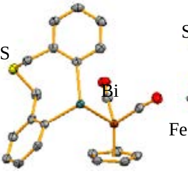

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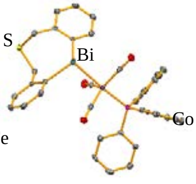

3

[1] T. Ollevier, E. Nadeau, *J. Org. Chem.* **2004**, *69*, 9292-9295; H. Sun, R. Hua, S. Chen, Y. Yin, *Adv. Synth. Catal*. **2006**, *348*, 1919-1925.

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Platinum-loaded microbubbles for the ultrasound-triggered treatment of brain cancer

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Tumors of the central nervous system are among the most disabling and lethal types of cancer.[1] Because of their depth and location in functional inoperable areas, some brain cancers are surgically unreachable. Therefore, only standard treatment such as chemo- and/or radiotherapy are possible. Anti-cancer drugs are designed to kill malignant cells, but when administrated, only a small fraction of the injected dose reaches the target site, with the rest circulating through healthy tissue, resulting in dose-limiting side efffets. Encapsulation of drugs within microbubbles combined with local release triggered by focused ultrasound is thought to increase their local concentration at the site of disease while minimizing side effects on healthy tissue.[2,3]

In this context, our group investigates microbubbles, gas-filled colloidal particles with a size range between 1-8 µm, also well-known as ultrasound contrast agents for imaging and diagnosis.[4] The work to be presented here is focused on the encapsulation of different platinum-based drug candidates within the microbubbles, study of their stability and payload delivery *in vitro* under application of ultrasound as an external stimulus.

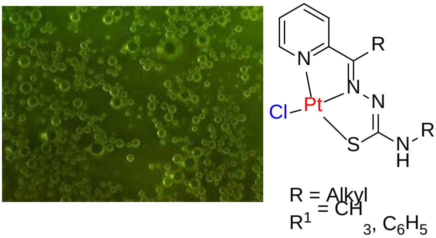

Figure 1: Fluorescence microscopy picture of stained microbubbles (left) and general structure of cytotoxic platinum complexes used in the context of this work (right)

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Coordination compounds acting as dielectrics for improving microelectric components

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Depending on their properties complexes, coordination polymers (CPs) and Metal-Organic Frameworks (MOFs) gained a huge scientific and economical interest for applications like gas storage[1] catalysis[2] or luminescent sensors,[3] whereas a possible usage of coordination compounds as dielectric components (see fig. 1, top) is a relatively young field of research.

Several investigations have shown highly interesting and unexpected results concerning the permittivity ε of coordination compounds. For example complexes, with many degrees of freedom, can show a high permittivity such as [MnCl$_2$(TzH)$_4$], (TzH = 1,2,4-1*H*-triazole) as well as an unexpected low ε (e.g. [ZnCl$_2$(TzH$_2$)]).[4] *Vice versa* a low ε (e. g. ZIF-8, see fig. 1, bottom)[5] as well as an unexpected high ε (e.g. ${}^{3}_{\infty}$[CdCl(H-TBP)], H-TBP = N-(4-(1*H*-tetrazol-5-yl)-benzyl)proline) have been found for more rigid CPs.[6] Obviously the dielectric properties cannot be predicted easily, wherefore the study of structure-property relationships is crucial for a deeper understanding of involved processes.

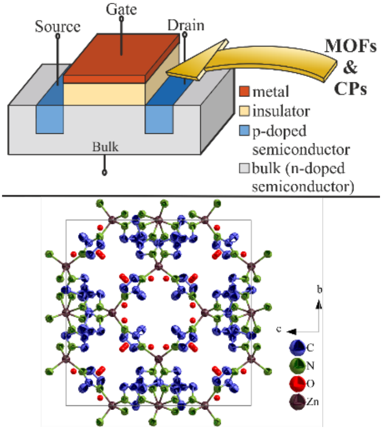

Figure 1: Schematic layout of a MISFET (top) and excerpt of the crystal structure of ZIF-8.[7]

[1] S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew.Chem. Int. Ed.* **2004**, *43*, 2334.

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Inorganic-Organic Hybrid Materials

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The focus of our research is on inorganic-organic hybrid materials. These are based on solid-state chemistry consisting of various fields like complexes, coordination polymers (CPs), metal organic frameworks (MOFs) and composite materials. We generate new hybrid materials with advanced properties such as effective tuneable luminescence or selective porosity for applications in various fields. This includes the development of substituents for Ln-based phosphors as well as new high-*k* or low-*k*-materials. Moreover, multifunctional composites for medical applications can be obtained by loading MOFs with active substances. We specialise in wide range of synthesis strategies such as solvent-free melt synthesis, mechanochemical, ionothermal and solvothermal synthesis. Using a modular chemical assembly approach with various metal precursors (main group-, transition-, rare earth-) and organic linkers (amides, amines, carboxylic acids, heterocyclic systems, ionic liquids, borates) we synthesise new materials. Furthermore, new multifunctional hybrid materials and composites are obtained by combination of CPs with other functional materials.

After the characterisation of new compounds, our main purpose is the determination of their material properties. Luminescence properties are analysed by photoluminescence spectroscopy. For the measurement of the specific surface area of porous materials and physical gas adsorption, we use BET analysis. In addition, the dielectric properties of coordination compounds are determined by dielectric spectroscopy. Studies on thermal behaviour by simultaneous differential thermal analysis and thermogravimetric analysis complete the broad range of analytical methods we use in our group.

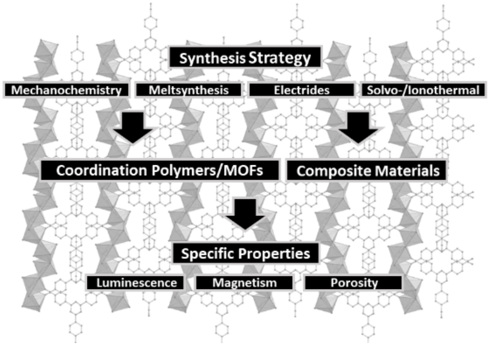

Figure 1. Synthetic approaches and research interests.

Ultra-narrow Bandwidth Organic Photodiodes by Exchange Narrowing in Merocyanine H- and J-aggregate Excitonic Systems

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The solid-state packing structure of π-conjugated organic molecules highly affects the materials' properties. For merocyanine dyes, usually arranging in an H-coupled antiparallel fashion,[1] more interesting J-coupling structures have rarely been reported. Here we show for nine highly dipolar merocyanines with the same π-scaffold and thus equal monomer properties in solution, that the packing arrangement can be controlled by the bulkiness of the donor substituent, leading to strong exciton coupling within a card stack (H) or zig zag (J) packing.[2] Both bands in the blue (H) and NIR (J) spectral ranges arise from a single exciton band. When used as organic photodiodes in planar heterojunctions with C60 fullerene, they show wavelength-selective photocurrents with external quantum efficiencies (*EQE*) up to 11 % and ultra-narrow bandwidths down to 30 nm.[3] Thus, narrowing the linewidths of optoelectronic functional materials by exciton coupling provides a powerful approach to yield ultra-narrowband organic photodiodes.

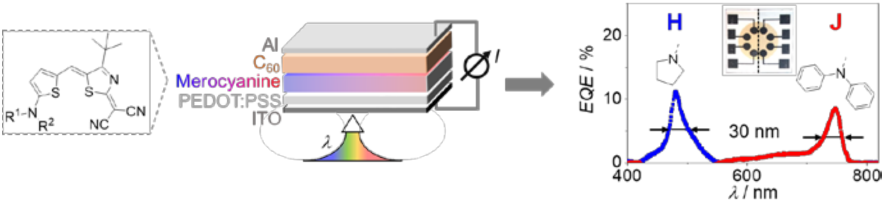

Figure 1. Application of merocyanine dyes in planar heterojunction photodiodes with corresponding *EQE* data of the best devices exhibiting an ultranarrow H- or J-band.

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Tetrahedral Cobalt NHC complexes and their use as ALD as well as low temperature CVD precursors

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The technique of chemical vapor deposition (CVD) has been known since the late 1950 as an efficient method for the deposition of thin films.[1] As a further development of this technique atomic layer deposition (ALD), elaborated in the late 1970s, offers a promising alternative and novel benefits in comparison to CVD and is nowadays already used for the fabrication of microelectronic devices.[2]

We present here the syntheses of a variety of NHC stabilized cobalt carbonyl nitrosyl complexes of the type [Co(CO)(NO)(NHC)$_2$] and [Co(CO)$_2$(NO)(NHC)] (NHC = *i*Pr$_2$Im, *n*Pr$_2$Im, Cy$_2$Im, Me$_2$Im, *i*Pr$_2$ImMe, Me$_2$ImMe, Me*i*PrIm, Me*t*BuIm; R$_2$Im: 1,3-dialkylimidazolin-2-ylidene).[3] These complexes have chemical and physical properties which make them suitable as precursors for any type of vapor deposition.

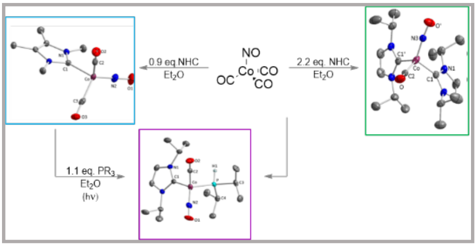

Figure 1. Syntheses of NHC stabilized cobalt carbonyl complexes of the type [Co(CO)(NO)(NHC)$_2$] and [Co(CO)$_2$(NO)(NHC)], as well as asymmetrically substituted cobalt phosphine complexes of the type [Co(CO)(NO)(NHC)(PR$_3$)].[3-4]

In general, low weight molecules typically reveal high volatility in many cases, which is an important feature for a CVD or ALD precursor. In addition, asymmetric molecules often possess low sublimation and melting temperatures, because of their high vapor pressure. Thus, the synthesis of novel asymmetrically substituted cobalt complexes of the type [Co(CO)(NO)(NHC)(PR$_3$)] (NHC = *i*Pr$_2$Im; PR$_3$ = PMe$_3$, PEt$_3$, PH*i*Pr$_2$; PR$_3$ = PMe$_3$; NHC = Me$_2$ImMe, Me*i*PrIm, Me*t*BuIm, *i*Pr$_2$ImMe; R$_2$Im: 1,3-dialkylimidazolin-2-ylidene), based on the reaction of the one-fold NHC substituted precursor and the corresponding phosphine, is also presented.[4]

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Synthesis of Pd(II) and Pt(II) complexes with functionalized triazolate ligands by iClick reactions

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Inspired by the success of cisplatin in the clinical treatment of various types of malignancies, the chemistry of metal-based drugs has received enormous attention in recent years. However, the effectiveness of metal-based compounds as antitumor agents is often hampered by their poor water solubility, low bioavailability, and lack of target specificity. Inorganic click (iClick) reactions,[1] which allow easy tuning of the bioavailability and ADMET (absorption, distribution, metabolism, excretion, toxicity) properties of novel compounds for bioactivity studies, can be utilized for a modular access to molecular diversity in transition metal complexes with novel structural motifs. In this work, a series of Pd(II) and Pt(II) triazolate complexes was successfully synthesized from the corresponding azide compounds and electron-deficient alkynes by the catalyst-free iClick [3 + 2] cycloaddition reaction (**Fig. 1**). The trifluoromethyl group of the alkyne serves as a sensitive ^{19}F NMR marker to monitor the progress of the reaction and allows studies of reaction kinetics and stereochemical preference.[2]

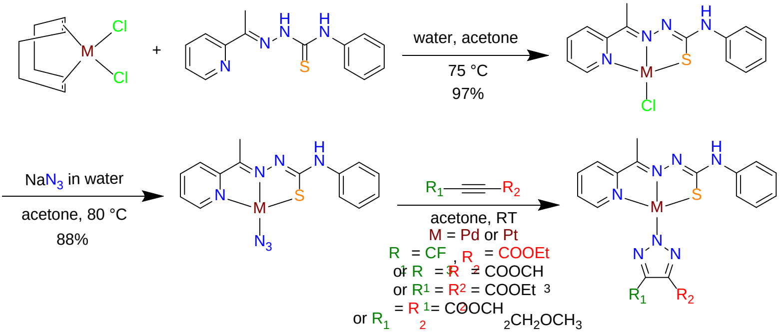

Figure 1. Synthesis of Pd(II) and Pt(II) triazolate complexes by iClick reactions.

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Professionalisierung durch Praxisbezug im Lehr-Lern-Labor

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Untersuchungen zeigten, dass es keinen Zusammenhang zwischen der Diagnosekompetenz von Lehrkräften und ihrer Berufserfahrung gibt [1]. Daraus lässt sich schlussfolgern, dass angehende Lehrkräfte ihre Diagnosekompetenz im Rahmen der Ausbildung erwerben. Allerdings wurde belegt, dass die Diagnostik der Lehrkräfte während des Unterrichtens in der Regel beiläufig erfolgt und auf subjektiven Urteilen beruht [2]. Erstrebenswertes Ziel der universitären Ausbildung muss daher sein, die Lehramts-Studierenden zu einer systematischen professionellen Reflexion zu befähigen. Hierzu müssen sie das Umsetzen von Handlungsmustern einerseits und die dazu führende professionelle Reflexion andererseits erlernen. Um dies zu erreichen, wurden theoriegeleitet Reflexions-Werkzeuge entwickelt. Im Rahmen eines Lehr-Lern-Labor-Seminars werden Lehramts-Studierende in deren Nutzung geschult, während sie Experimentierstationen entwickeln und Schüler bei der Durchführung der Experimente betreuen.

[1] Hesse, I., Latzko, B. (2017). Diagnostik für Lehrkräfte. Stuttgart: utb.

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Organometallic indole derivatives as a new way to label proteins

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Artificial protein modification with organic or organometallic groups allows the introduction of new functionalities to such biomacromolecules. Preferred are bioorthogonal reactions which do not undergo side reactions with other functional groups present in a particular biological system.[1-3] Recently, an interesting new way was reported to modify the ε-amino groups of lysine residues in lysozyme in a Mannich-like reaction with indole derivatives under retention of the native charge.[4]

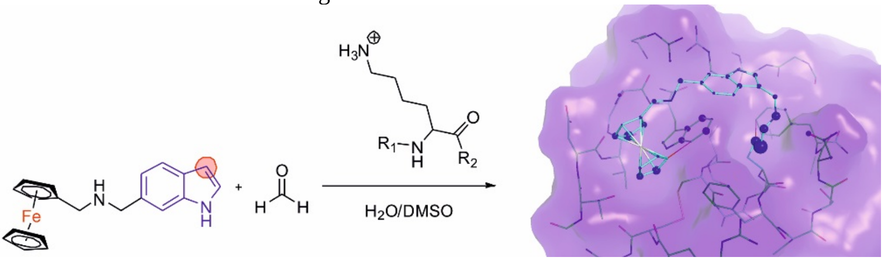

Fig. 1: (Left) Reaction of *N*-ferrocenylmethyl-6-aminomethylindole with formaldehyde and lysozyme and (right) most preferred pose of the conjugate after docking with GOLD.

To extend that method to organometallic protein labelling, we have synthesized a family of indole conjugates with cymantrene ($CpMn(CO)_3$), cyrhetrene ($CpRe(CO)_3$), and ferrocene (Cp_2Fe) groups attached to different positions on the 6-membered ring of indole to study their conjugation efficiency to lysozyme and compare it to commercially available organic indoles. Conjugate formation was analyzed with ESI mass spectrometry. In addition, covalent docking simulations were carried out to determine the most accessible lysine side chains and to elucidate the steric influence of the protein surface as well as that of the indole derivatives through the empirical scoring functions ASP and DSX in GOLD.

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Lichtstimulierbare, flüssigkristalline Azofarbstoffe mit Peptidanker – eine synthetische Herausforderung

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Flüssigkristalline Verbindungen (Mesogene) finden aufgrund ihrer Fähigkeit zur Selbstorganisation vielfältige Anwendungen nicht nur in der Technik (LC-Displays) sondern auch in der Natur (z.B. in Spinnfäden oder Zellmembranen). Raumfüllung, Nanosegregation und die Feineinstellung von spezifischen Wechselwirkungen steuern dabei das Verhalten in den weichen Materialien, die gleichzeitig anisotrope und fließende Eigenschaften verbinden. Eine der wichtigsten spezifischen supramolekularen Wechselwirkungen ist die Wasserstoffbrückenbindung. Durch geschicktes Moleküldesign kann diese genutzt werden um neuartige Mesophasen zu induzieren und zu stabilisieren.[1]

Das Ziel dieser Arbeit ist es, lyotrope Peptidflüssigkristalle mit einer zentralen Azobenzoleinheit zu präparieren, die als lichtinduzierte artifizielle Muskeln genutzt werden können. Dabei soll ein Azofarbstoff über lange aliphatische Spacer eingefügt werden. Die Tripeptide befinden sich an beiden Enden des Moleküls (Abbildung 1) und werden mittels Festphasenpeptidsynthese aufgebaut. Diese sollen in einer lyotropen Mesophase die erforderlichen Netzwerkverknüpfungen über Wasserstoffbrücken gewährleisten. Die Synthese birgt mehrere Herausforderungen, die im Detail diskutiert werden sollen. Die präparierten Verbindungen **1** werden des Weiteren mittels verschiedener Methoden auf ihre Flüssigkristalleigenschaften untersucht.

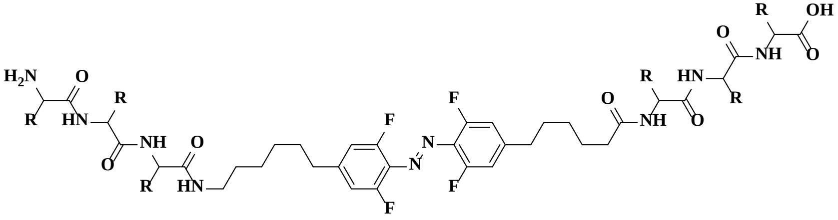

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Abbildung 1. Zielverbindungen

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Perfluoroalkylhydridoborane Adducts

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Hydridoboranes are well known as Lewis acidic reagents for synthesis. Especially, adduct formation is quite familiar with this substance class. E.g. the adduct formation with amines leads to amine boranes which are well-known for their potential hydrogen storage ability.[1] Moreover *N*-heterocyclic carbenes (NHCs) have been shown to form for example NHC-BH_3.[2] Perfluoroalkylboranes have been found to give a variety of stable adducts with different bases. Examples include the unusual borane carbonyl $(CF_3)_3BCO$ [3, 4]or the ammine complex $(CF_3)_3BNH_3$ [5]and the acetonitrile adduct $(CF_3)_3BNCCH_3$.[6]

Recently, the perfluoroalkylhydridoborate anion $[C_2F_5BH_3]^-$ has become available that serves as a starting material for borane adducts of the type $C_2F_5BH_2$–L.[7] The bases studied, so far, include phosphanes, NHCs, silylenes and cyclic (amino)(alkyl)carbenes (cAACs). Most of these adducts have been characterized by single-crystal X-ray diffraction and a number of spectroscopic methods. First results on the follow-up chemistry of these adducts will be presented, as well.

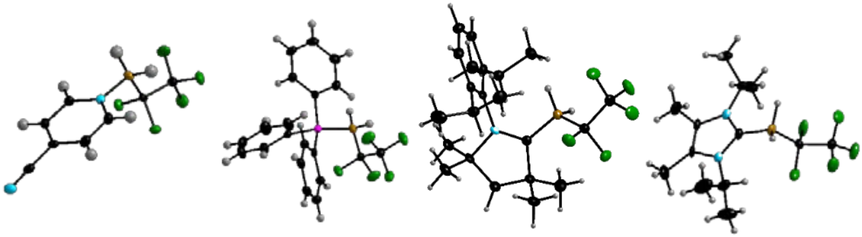

Figure 1: Selected perfluoroalkylhydridoborane adducts with selected Lewis bases: 4-CN-Pyridine, PPh_3, cAAC, NHC (from left to right).

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Dye-Containing Covalent Organic Frameworks

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Due to their extended π-conjugated molecular scaffolds and visible light absorption abilities, organic dye molecules have been widely incorporated in organic electronic and photovoltaic devices such as organic field effect transistors (OFETs) or organic solar cells (OSCs). Since their performances are strongly influenced by the molecular arrangement of the active components, the implementation of organic dyes as building blocks into crystalline, two-dimensional polymers, e.g., covalent organic frameworks (COFs), makes such materials promising candidates for electroactive materials.[1]

In search of novel porous materials, we here report the formation of dye-containing donor-acceptor COFs by means of dynamic covalent chemistry of diketopyrrolopyrrole (DPP) derivatives and tetraaminophenylporphyrins (TAPP).[2] DPP-TAPP-COF shows enhanced light harvesting in the visible region and spontaneously self-assembles into tubular arrangements.

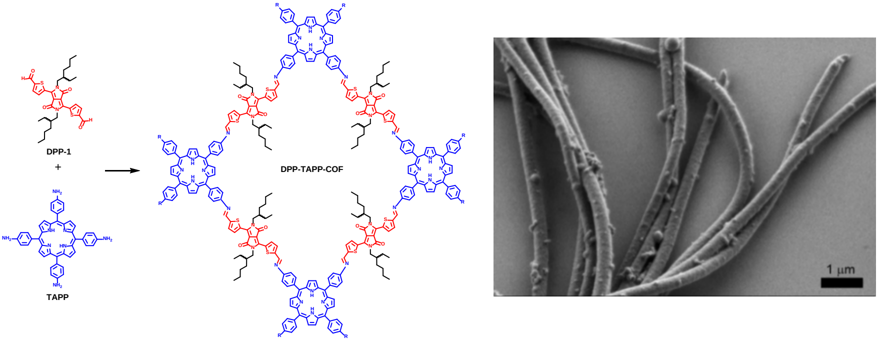

Figure 1. DPP-TAPP-COF and SEM image of the tubular arrangement.

References:

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[2] B. Gole, V. Stepanenko, S. Rager, D. D. Medina, T. Bein, F. Würthner, F. Beuerle, *Angew. Chem. Int. Ed.* **2018**, *57*, 846–850.

A monolithic setup for investigation of ultrafast phenomena at the nanoscale

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Ultrafast spectroscopy is a well-established technique to obtain information about processes occurring on extremely short timescales. We use a non-collinear optical parametric amplifier system to create a pair of individually tunable femtosecond pulses with central wavelengths ranging from the ultraviolet to the near-infrared. On top of that, we combine our laser pulses with an aberration-corrected photoemission electron microscope (PEEM) to go beyond the optical diffraction limit and to get detailed insights into ultrafast physics (sub 20 fs) occurring on the nanoscale (sub 5 nm). By creating complex laser pulse sequences, it is further possible for us to probe coherent phenomena happening on the nanoscale [1]. In this poster we want to showcase the versatility of our setup by presenting several projects, ranging from metallic nanostructures to biological samples (Fig. 1).

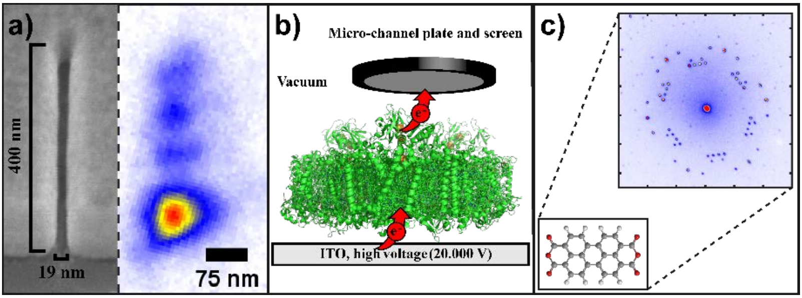

Figure 1. a) SEM Image of a plasmonic gold nanoslit resonator, as well as a typical imaged photoemission pattern. **b)** Investigation of electron transport in cyanobacterial Photosystem I on a conductive surface with PEEM. **c)** PTCDA thin film deposited in vacuum and characterized with low energy electron diffraction.

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Hydrogel-coating of polymers in a customized 3D-printed reactor via SIPGP

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Surface engineering is a very important discipline nowadays, because many products need a coating to deal with the environment they are exposed to. Here hydrogels are manufactured as a coating for biomedical applications. To achieve that, a technique called SIPGP (Self-Initiated PhotoGrafting and Photopolymersization) is used. That technique allows the omission of additional photo-initiators for the photochemical polymerization of the hydrogel, whereas the hydrogel is covalently bond to the coated surface. [1] In addition, the monomers used are methacrylates (e.g. Hydroxytheylmethacrylate (HEMA)) which are water-soluble, so that the whole process is free of organic solvents. These facts make SIPGP highly suited for the coating of biomedical applications.

As substrates MEW-printed poly(caprolactone) (PCL)-scaffolds and poly(vinylidenfluoride) (PVDF)-Terpolymer-Films are used. To achieve a reaction in a constant monomer-flow, specially designed and 3D-printed reactors are used. The setup for the reaction can be seen in Fig. 1.

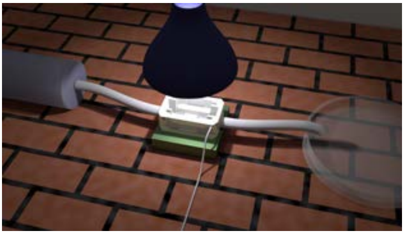

Figure 1. Reaction setup for the constant flow with a syringe-pump left-handed an outlet right-handed a UV-Lamp on the top, argon-inlet at the bottom of the picture and the reactor in the middle.

Measurement of the system can be done for example with SEM, fluorescence microscopy or contact-angle, because of the surface getting more hydrophilic by being coated.

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Polymer-Drug Specificity in Drug-loaded poly(2-oxazoline) and poly(2-oxazine) micelles

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According to estimates, more than 40% of all new chemical entities discovered in the pharmaceutical industry are practically insoluble in water. This illustrates the urgent demand for excipients, which increase the water solubility of such hydrophobic drugs. Motivated by the extremely high drug contents of poly(2-oxazoline) (POx) based micelles for paclitaxel (PTX) of more than 45 wt.%[1], this study investigates the incorporation of the hydrophobic molecules curcumin (CUR) and PTX into POx and poly(2-oxazine)s (POzi) with various chemical structures. Unexpectedly, even very small structural changes within the polymer amphiphile strongly affected the drug-polymer compatibility.[2] With the most compatible polymer, CUR-loading of more than 50 wt.% were feasible. As conventional 2D cell cultures suffer major limitations in predicting future treatment outcomes, 3D-tissue models with breast cancer cells MDA-MB-231 cells were examined.[3] An increased resistance of the breast cancer cells in the 3D tissue models was observed (Figure 1). As stability in complex biological media was higher for nano-formulated CUR than for DMSO/CUR, the ultra-high drug-loaded nanoformulation might allow high-dose *in vivo* therapy necessary for effective therapeutic high-dose intervention.

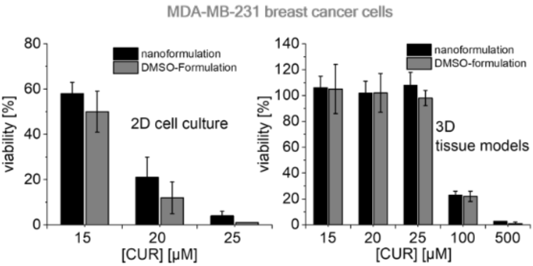

Figure 1. Cytotoxicity of nano-formulated CUR and DMSO/CUR in 2D-cell culture and 3D-tissue models of MDA-MB-231 cancer cells.[3]

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[2] M. M. Lübtow *et al. JACS*, **2017**, *139*, 10980
[3] M. M. Lübotw *et al. ChemXriv*, https://doi.org/10.26434/chemrxiv.5661736.v1

Improved understanding of Micelle-encapsulated Curcumin by NMR Spectroscopy

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The natural product curcumin shows various biological and pharmacological activities, e.g. anticancer activity and suppression of epithelial–mesenchymal transition.[1] Unfortunately, curcumin also exhibits poor aqueous solubility and thus a low bioavailability. To overcome this barrier for drug delivery, micellar formulations of curcumin (Cur) and a polymer (KRM06, Figure 1) are used in this project. Previously, the Luxenhofer group observed, that increasing the amphiphilic contrast between the polymer blocks (CH_3 vs. C_9H_{19}) does not increase the curcumin loading.[2]

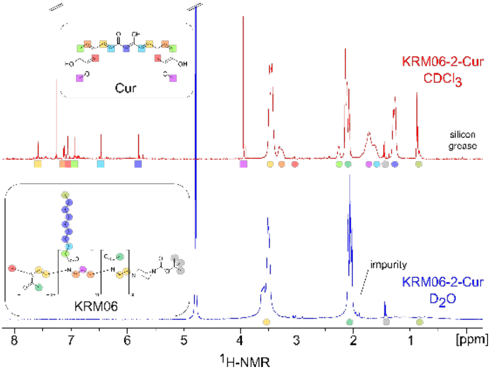

Figure 1. Comparison of the ^1H NMR spectra of a curcumin-polymer-formulation in $CDCl_3$ (red) and in D_2O (blue).

To improve our understanding of molecular features and corresponding drug loadings, the pure polymer, pure curcumin and its formulations are investigated using 1D and 2D liquid and solid-state NMR experiments.

In first experiments, we could analyze the micelles in aqueous solution and compare the radii determined by NMR diffusion experiments with values obtained from DLS.[2] Further insight into the curcumin-polymer-interactions can be obtained by solid-state NMR experiments. In solution, the incorporated curcumin can't be observed due to the reduced mobility of the drug molecules inside the comparably rigid core of the polymer.

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Synthesis and Characterization of NIR Dye-Doped Nanoparticles for in vivo Medical Imaging

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Nanoparticles (NPs) are promising tools for a wide spectrum of biological and medical applications. They can be used as carrier and delivery systems for active agents such as biomolecules, dyes and a wide range of sensitive substances and also contribute to the stabilization of these compounds in vivo. Real time non-destructive imaging screening in vivo can be performed by means of fluorescent based methods.

Here, we present our recent research activities in the field of medical diagnostics concerning the encapsulation of NIR dyes, e.g. Indocyanine Green (ICG) and IRDye® 800CW, into NPs for in vivo imaging. Our work is focused on the synthesis and characterization of NP carrier systems on the basis of various carrier systems, e.g. amorphous silica and liposomes. These NPs are synthesized via wet-chemical synthesis and doped with different NIR dyes. The choice of silica and liposomes as a basis of the NPs is motivated by their high biocompatibility, biodegradability and the possibility of surface modifications. The focus here was on the investigation of stability of the encapsulated NIR dyes under different storage and physiological conditions. In addition to greater stability, the photoacoustic effect of NIR dye doped NPs has been demonstrated.

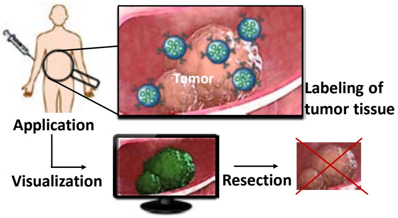

Figure 1. Visualization of tumor tissue by NIR dye-doped nanoparticles

In summary, the synthesis of different NP systems on the basis of amorphous silica and liposomes and the encapsulation of different NIR dyes was successfully demonstrated. With the confirmation of the stability of the encapsulated dyes in the NP matrix and their photoacoustic activity they have shown their potential in the field of medical imaging.

NHC-Nickel-catalyzed borylation of polyfluorarenes via C–F bond cleavage

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The selective synthesis of fluorarene compounds has become a subject of growing interest due to the prominent role such species play in many modern pharmaceuticals, agrochemical and other industrally important products.[1] An attractive strategy is the use of fluorinated boronic acids or boronate esters, which are versatile reagents in organic synthesis such as the widely employed Suzuki-Miyaura coupling reaction. The transition-metal-catalyzed borylation of aryl halides has emerged as one of the most important mild and attractive route for the synthesis of arly boronates in recent years.[2] The conversion of fluoroaromatics into arylboronic esters via C–F bond activation is relatively unexplored and was restricted to noble metal catalysts until recently.[3] This presentation covers the synthesis and reactivity of NHC-stabilized nickel complexes in stoichiometric and catalytic C–F bond activation of polyfluoroaromatics and their use in catalytic borylation as well as mechanistic studies.[3f]

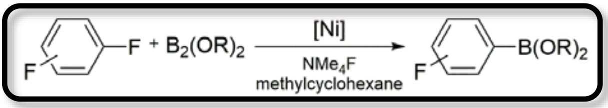

Figure 1. NHC-Nickel-catalyzed borylation of polyfluorarenes via C─F bond cleavage.

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A focus on the drug sphere: CORM conjugation to biomolecular carrier systems

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As a colorless and odorless gas, carbon monoxide (CO) is generally known to the public as the "silent killer". However, it is generated in living organisms from the degradation of heme by heme oxygenase (HO) enzymes. It dilates blood vessels and possesses anti-inflammatory and anti-apoptotic as well as cytoprotective properties.

The key problem in the therapeutic application of CO is to find novel delivery systems for specific tissue accumulation. *CO-releasing molecules* (CORMs) are metal carbonyl complexes which have the potential for facile CO delivery that can be controlled in a spatial and temporal manner. In this context, functionalized light-triggered CORMs (PhotoCORMs) conjugated to biomolecular carrier systems are developed and characterized for various applications (Fig. 1).[1-3]

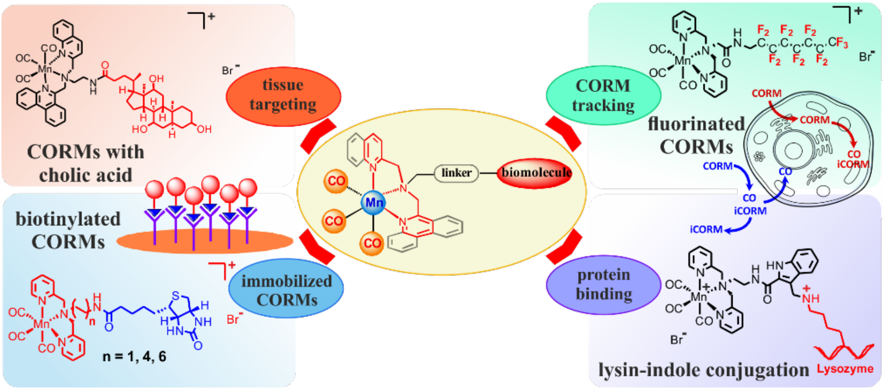

Figure 1. Applications of PhotoCORMs conjugated to (bio)molecular carrier systems.

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Theoretical Methods For The Study Of Supramolecular Aggregation Mechanisms

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The theoretical investigation of supramolecular aggregation is a demanding task, especially regarding systems that exhibit polymorphism. Kinetic models have been used to classify aggregation mechanisms according to their cooperative, anticooperative, or isodesmic nature. However, sophisticated simulations are necessary in order to identify the species present in solution and to explain which of them are formed under specific conditions. As a robust method to determine the minimum energy pathway of a transition, we employ the nudged elastic band method.[1] The initial guess of the transition pathway is obtained by molecular dynamics modified by a repulsive potential dependent on the RMSD-value with respect to a reference structure. The optimized minimum energy pathway provides information on the underlying mechanistic steps and the corresponding transition barrier.

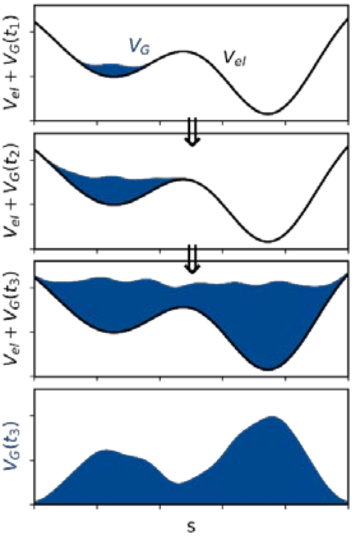

Figure 1. Scheme of the metadynamics enhanced sampling method based on a history dependent bias potential.

By combination of this technique with the metadynamics formalism[2] (see Fig. 1), our aim is to evaluate the free energy surface including the dynamics of molecules in solution.

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Dualsteric targeting of muscarinic receptors – Synthesis of M_2/M_4 subtype selective hybrid ligands

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The action of acetylcholine as neurotransmitter in the central nervous system is mediated by five subtypes of muscarinic acetylcholine receptors (mAChRs). Compounds that target mAChRs often lack subtype selectivity due to the highly conserved orthosteric binding site of acetylcholine.[1] This issue has been faced with the development of selective molecules addressing a topologically distinct and thereby less well conserved allosteric site of mAChRs.

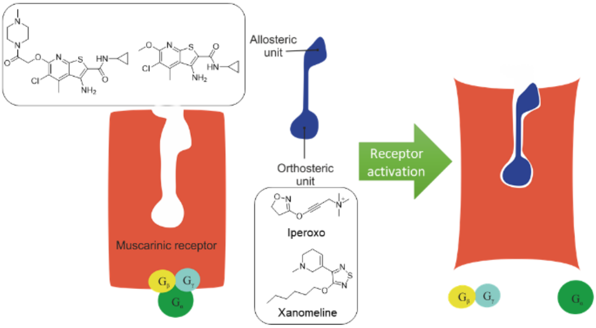

Figure 1: Muscarinic receptor activation by dualsteric hybrid ligands.

Allosteric ligands can form a ternary complex in combination with an orthosteric agonist. This allows modulation of the receptor activity by either enhancing or diminishing the maximum effect.[2] Alternatively, a dualsteric approach can be pursued by combining an allosteric and an orthosteric ligand within one molecule. In this context we focused on the design of M_2 and M_4 preferring hybrid compounds. We study the linkage of iperoxo or xanomeline as orthosteric units with different thieno[2,3-b]pyridine derivatives, that were identified as allosteric modulators in a small molecule screening for the M_4 receptor.[3] These hybrids may allow new insights into mechanisms of mAChR-activation.

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Erschließung innovativer chemischer Kontexte mithilfe spektroskopischer Techniken

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Spektroskopische Techniken basieren auf der Wechselwirkung zwischen Licht und Materie, wodurch qualitative und quantitative Aussagen über Proben und deren Inhaltsstoffe getroffen werden können [1]. Durch die damit verbundene Vernetzung von Grundprinzipien der Physikalischen Chemie mit Anwendungen der chemischen Analytik lassen sich innovative Kontexte für Lernende zugänglich machen. Experimente im sichtbaren Wellenlängenbereich des elektromagnetischen Spektrums eröffnen zusammen mit der Erkundung spektraler Bauteile eines UV/Vis-Spektrometers einen phänomenologischen Zugang zur Thematik [2].

Im Rahmen dieses Beitrages werden alltagsnahe Kontexte vorgestellt, die durch Emissions- und Absorptionsmessungen erschlossen werden können. Im Bereich der Scheinwerfertechnik gab es in den letzten Jahren zahlreiche Innovationen, weshalb die klassischen Halogenscheinwerfer häufiger durch Xenon-, LED- oder sogar Laserscheinwerfer (siehe Fig. 1) ersetzt werden. Eine Analyse der Emissionsspektren lässt Rückschlüsse auf die ablaufenden chemischen und physikalischen Vorgänge in den verschiedenen Leuchtmitteln zu.

Figure 1. Modell eines Scheinwerfers mit Lasertechnik

Mit Absorptionsmessungen lässt sich das anschauliche und lehrplanrelevante Thema „Farbstoffe“ erschließen. Insbesondere der Einsatz von Azofarbstoffen in Lebensmitteln wird vielfach kontrovers diskutiert. Bei Jugendlichen beliebte Getränke werden häufig mit diesen Farbstoffen versetzt um sie optisch ansprechender zu machen. Die Extraktion der Farbstoffe aus Getränken und deren anschließende qualitative und quantitative Analyse verbindet Techniken der nasschemischen Analytik mit Messmethoden der optischen Spektroskopie.

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Diborene: Generation and Photoelectron Spectroscopy of an Inorganic Biradical

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2 Institut des Sciences Moléculaires d'Orsay, CNRS, Bât. 520 Université Paris-Sud and Paris-Saclay, F-91405 Orsay Cedex
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Up until now biradicals mostly represent a little understood curiosity among improving concepts of chemical bonding. It is predicted that simple diborenes R-B-B-R' avoid double bonding and exhibit a triplet ground state, therefore being representatives of the intriguing group of biradicals.[1] In this work we were able to synthesize the simplest diborene HBBH in the gas phase, utilizing the H-atom abstraction of diborane by fluorine radicals (Scheme 1). Since the abstraction of H-atoms is highly unselective many different B_2H_x species were present next to HBBH. We therefore applied photoelectron photoion coincidence spectroscopy allowing us to record mass-selective photoelectron spectra. The HBBH was ionized using the vacuum ultraviolet radiation provided by the DESIRS beamline at the synchrotron SOLEIL in Paris, France. The vibrational progression visible in the photoelectron spectrum is corresponding to the B-B stretching vibration. In collaboration with the group of Roland Mitric we were able to investigate the cation more precisely revealing two Renner-Teller split doublet states, which are also visible in the experimental spectrum.[2]

$$B_2H_6 + 4\,F \longrightarrow HBBH + 4\,HF$$

Scheme 1: Generation of diborene from diborane using H-atom abstraction by fluorine atoms

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[2] D. Schleier A. Humeniuk, E. Reusch, F. Holzmeier, D. Nunez-Reyes, C. Alcaraz, G. A. Garcia, J-C. Loison, I. Fischer, R. Mitric *J. Phys. Chem. Lett.* **2018**, *9*, 5921-5925

Multifunctional molecular materials for the interaction of magnetism and luminescence

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The aim of the project is to combine both luminescence and magnetism by providing a rational design of coordination polymers of 3*d*- and 4*f*- metal ions, including metal-organic frameworks (MOFs) containing defined molecular blocks. Interaction of luminescent and magnetic species will be investigated on the feasibility to generate sensors for magnetic states by an observable change in the luminescence properties.

A lanthanide novel coordination polymer (Fig.1) was synthesized from anhydrous $TbCl_3$ and 3-(1H-Pyrazol-3-yl)Pyridine (PzPy) under solvothermal conditions in Toluene. The characterization of these novel compounds are now performed utilizing different techniques followed by the determination of relevant Luminescence properties.

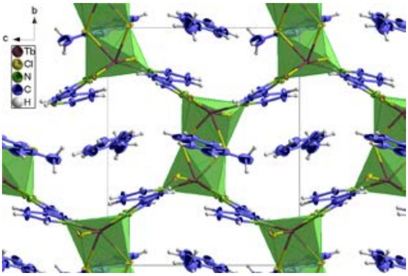

Figure 1. The crystal structure of a novel coordination Polymer from a reaction of $TbCl_3$ and PzPy with a view along [001]

The results will be gathered and evaluated to achieve both fundamental knowledge on the options to combine magnetism and luminescence as well as potential new applications in sensing and detection. This kind of sensing includes detection that can in principle be easily observable by the eye such as defined changes in the luminescence by interaction with a certain analyte gas or liquid molecule as well as, of course, a magnetic metal ion.

The option to sense an analyte by a change in the luminescence properties has inspired MOF chemists very recently and is a present focus of MOF chemistry[1], as it can be used to monitor both the presence of chemical species and processes and physical parameters like temperature[2].

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Reacitivity of NHC stabilized Alanes

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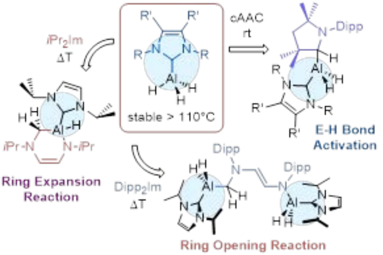

Figure 1. Ringexpansion-, ringopeningreaction and Al-H-bond activation of $(NHC)\cdot AlH_3$.

NHCs show a broad reactivity towards main group element hydrides and organyls.[1] We and others demonstrated earlier, that in dependence on the electronic and steric properties of the carbene and on the main group element compound used, various reaction channels can be observed. It was demonstrated earlier, that cyclic (alkyl)(amino) carbenes (cAACs) provide a robust environment for Si-H, B-H, P-H, C-H and even C-F[2] bond activation. For the reactivity of NHCs with *Lewis* acidic hydrides such as silanes[3], boranes[4] and beryllium hydrides[5] ring expansion of the NHC can be observed. The different reaction pathways show the importance of the used carbene. NHC aluminium chemistry is developed to some extend and it is known that *Lewis* acid-base adducts of aluminium hydrides are rather unstable. We decided to take a closer look on the behavior of carbenes with aluminium hydrides. The synthesis of the mono NHC alane adducts $(NHC)\cdot AlH_3$ as well as their reactivity towards different types of carbenes and fluoraromatics is presented. While the mono NHC adducts remain stable at elevated temperatures, ring expansion reaction occurs when $(iPr_2Im)\cdot AlH_3$ is reacted with a second equivalent of the carbene. In contrast, ring opening is observed with sterically more demanding $Dipp_2Im$. The reaction of $(NHC)\cdot AlH_3$ and $(iPr_2Im)\cdot AliBu_2H$ with $cAAC^{Me}$ yields instead to an insertion of the carbene carbon atom into the Al–H bond.[6] We also report first results of the utilization of NHC-stabilized alane adducts $(NHC)\cdot AlH_3$ and $(NHC)\cdot AliBu_2H$ as novel hydride transfer reagents in the hydrodefluorination (HDF) of different fluoroaromatics and hexafluoropropene.[7]

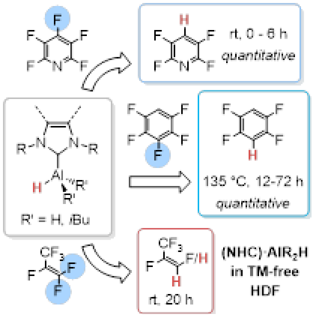

Figure 2. Hydrodefluorination (HDF) of fluoroaromatics and hexafluoropropene with $(NHC)\cdot AlH_3$.

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Fluorescent artificial nucleosides

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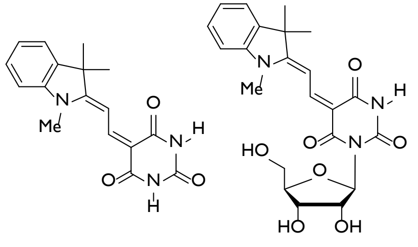
Fluorescent nucleosides are chemically modified ribo- and deoxyribonucleosides with improved fluorescent properties for analysis of DNA and RNA. Maintaining the chemical and biological functionalities, these analogs are useful emissive tools for examination of nucleic acid structures, locations and interactions at the molecular level. Since naturally occurring nucleosides are practically non-fluorescent, modifications on their structures are required and have led to a broad palette of fluorescent DNA and RNA analogues. Different methods for fluorescent labeling have been reported for the four canonical nucleobases and are also available for epigenetic and artificial derivatives.[1], [2]

Our goal is to expand on our previous work of generating hemicyanine dyes on modified uridines.[3] Here, we focus on labeling of 6-hydroxyuridine, which is a tautomer of N-ribosylated barbituric acid. For this purpose, synthetic pathways towards barbituric acid-derived cyanine dyes as well as the corresponding nucleosides were developed. The synthesized compounds were comprehensively characterized to gain more insight in their chemical and spectroscopic properties. Thus, a range of different measurements was performed such as pK_a-titrations and dilution series. The fluorescent properties seem to be promising for labeling oligonucleotides containing 6-hydroxyuridine since the fluorescence emission intensity of the nucleosidated derivatives is much higher than for the nucleobase analog alone.



1 2

Figure 1. Cyanine-labeled barbituric acid derivatives. Modified uracil nucleobase analog **1** and its β-D-riboside **2**.

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Direct Observation of Exciton-Exciton Interactions in Squaraine Copolymers

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Former studies showed that exciton-exciton annihilation is an important factor in squaraine copolymers because of the high exciton diffusion constant.[1] Investigating exciton-exciton annihilation with transient absorption techniques is challenging because it is not possible to measure a direct signature of this process. Our recently introduced technique of exciton-exciton-interaction two-dimensional (EEI2D) spectroscopy gives a direct access to the observation of the annihilation of excitons.[2] The fifth-order signal, which can be observed at twice the pump frequency, only occurs if exciton-exciton annihilation takes place in the sample and is easy distinguishable from single-exciton dynamics. In the present work we analyze the exciton dynamics in a series of squaraine copolymers with different chain lengths. Different timescales for exciton transport processes depending on the length of the chain could be identified and provide a better understanding of the fundamental processes occurring in this kind of polymers.

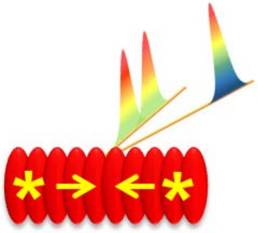

Figure 1. Scheme of the observation of exciton-exciton annihilation by coherent two-dimensional spectroscopy.

[1] S. F. Völker, A. Schmiedel, M. Holzapfel, K. Renziehausen, V. Engel, C. Lambert, *J. Phys. Chem. C*, **2014**, *118*, 17467-17482.

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Irreversible B-B Bond and Reversible B-C Bond Oxidative Addition at a Carbon Centre

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NHCs and related molecules can be employed in element-element bond activation processes, for example in the β-borylation of α,β-unsaturated compounds with diboron(4) compounds.[1,2] We recently reported a variety of NHC ring expansion reactions (RERs) of NHC adducts of diboron(4) compounds and other substrates as a result of E-E bond activation, which could impact upon the use of NHCs as organocatalysts.[3,4] Compared to NHCs, cAACs have a smaller HOMO-LUMO gap and are thus stronger electrophiles and nucleophiles.[5] These features enable cAACs to activate small molecules such as CO, H_2, P_4 and other enthalpically strong single bonds, such as B-H, C-H, and C-F.[5-8] These properties of the cAACs, i.e. enhanced electrophilicity and enhanced stability with respect to ring expansion, led us to investigate these molecules as prospects for carbon-element bond activation processes.[7] Here we show (i) irreversible oxidative addition of diboron(4) compounds to the cAAC carbene carbon atom, (ii) unique examples of reversible oxidative addition of organoboronate esters to the cAAC carbene carbon atom and (iii) the first example of a ring expansion reaction observed for a cAAC.[9]

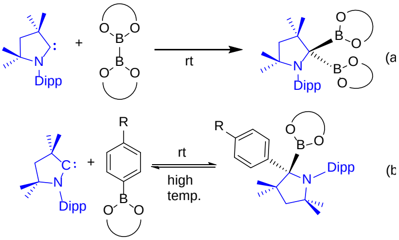

Figure 1. The reaction of $cAAC^{Me}$ with diboron(4) compounds (a) and arylboronic esters (b)[9]

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Synthesis and optical properties of 2,2'-ditetracene

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Singlet fission is a spin-allowed process in which a singlet state splits into two triplet states localized on two chromophores. The efficiency depends strongly on the relative orientation of the participating molecules. Tetracene, a polycyclic aromatic hydrocarbon (PAH) which consists of four linearly fused benzene rings, is classified as an open-shell system and is, due to its relatively small triplet excitation energies, a promising candidate for singlet fission.[1] To demonstrate the effect of molecular conformation on the progress of singlet fission 2,2'-ditetracene [2] was synthesized in a seven-step-synthesis via flash-vacuum-pyrolysis, Diels-Alder cycloaddition, halogenation and transition-mediated coupling reactions. The chromophores were forced into a particular conformation by the surrounding lattice (different crystalline and non-crystalline environments) to compare the optical properties of single tetracene and covalently linked ditetracene molecules.

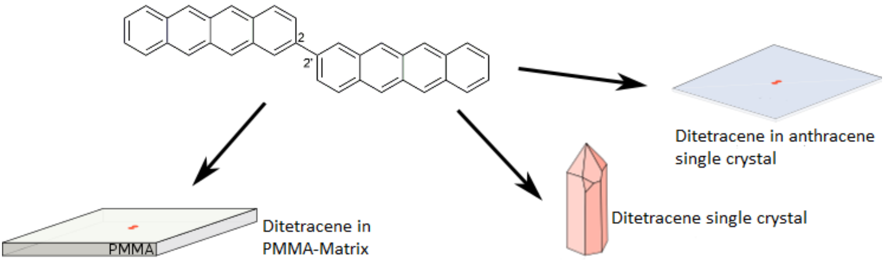

Figure 1. *Ditetracene doped into different crystalline and non-crystalline environments*

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Endohedral boron nitride nanotubes

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The use of fluorophores as markers in the life sciences fields often faces the challenge of fast photobleaching and limited chemical durability.

In this study, we plan to shield fluorophores such as α-Sexithiophene by encapsulation in boron nitride nanotubes (BNNTs) as illustrated schematically in figure 1. BNNTs are transparent in the visible region of the electromagnetic spectrum and they are inert to most acids and bases.[1] This is expected to allow protecting endohedral fluorphores against oxidation and photobleaching. Specifically, we plan to perform spectroelectrochemical investigations on bulk samples as well as on individual filled BNNTs to study their redox behavior and photochemical stability. To facilitate these experiments, we will develop and refine protocols for the preparation of dye filled BNNTs and modify an existing photoluminescence microscope and spectrograph for the investigation of these systems under potentiostatic control.

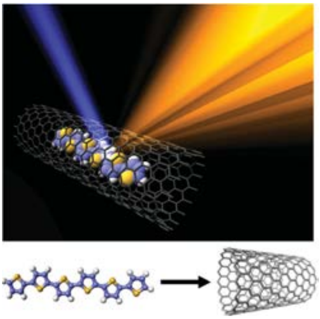

Figure 1. Schematic illustration of an encapsulated α-Sexithiophene molecule inside a BNNT.[2]

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[2] M. A. Loi et al. Adv. Mater. 2010, 22, 1635-1639

A New Synthetic Approach towards Polycyclic Aromatic Dicarboximides by a Palladium-Catalyzed Annulation Reaction

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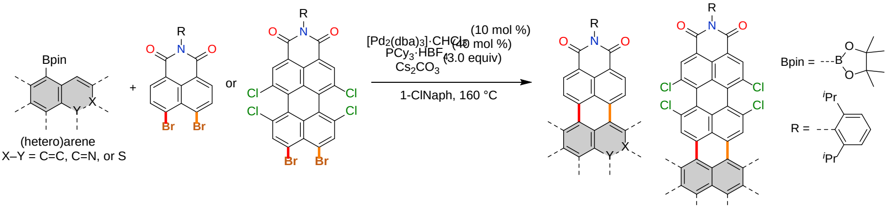
We have recently introduced a generalized synthetic route for the synthesis of electron-deficient polycyclic aromatic dicarboximides (PADIs) by an efficient C-C-coupling cascade reaction combining palladium-catalyzed Suzuki-Miyaura cross coupling and direct arylation starting from dibromo-naphthalene dicarboximides and planar or bowl-shaped aryl boronic esters.[1-5] This convergent synthetic route afforded a broad series of electron-deficient PADIs, including a novel C_{64} nanographene[1] and bowl-shaped PADIs[5]. Furthermore, our synthetic strategy can be applied for the synthesis of tetra-chlorinated PADIs starting from *peri*-dibrominated perylene imide derivative.[6] Only recently, we could extent the scope of this method for the synthesis of thiophene-annulated PADIs. Single crystals suitable for X-ray analysis were successfully grown for some of these molecules, confirming their π-extended aromatic geometries.



1 2 3 4 5

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Filling the Void:
New Hybrid Peptide/OPV Star-Mesogens

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The self-assembly of shape-persistent star mesogen **1** has been recently shown to be tunable by guest molecules, which fill the void space between the oligo(*p*-phenylenevinylene) arms [1,2]. Thereby the mesogens with bound “pseudo” guests (**2a-c**) reveal the highest mesophase stability, since the guests cannot escape from the intrinsic cavity [2]. This prompt us to study the impact of guests, which will not naturally incorporate by supramolecular interactions. There for we synthesized mesogens **3a-d** with oligopeptide building blocks. With these hybrid mesogens we aim to control the nanostructure of a segmented column. The mesophase properties as a function of the peptide length are studied by means of polarized optical microscopy, differential scanning calorimetry and x-ray diffraction.

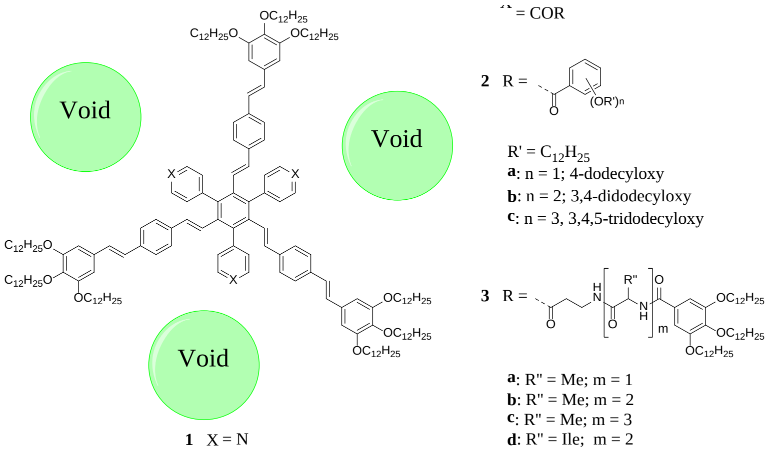

Figure 1. New hybrid Peptide/OPV star-mesogens.

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Luminescent Triarylborane-Based Chromophores for Biological Imaging

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Triarylboranes have found applications in many different fields, for example as anion sensors, OLED materials and as non-linear optical materials.[1] The extraordinary optical properties and exceptional stability of triarylboranes, which have been investigated and refined over the last two decades,[2] have motivated our group to utilise triarylborane-based chromophores for biological imaging applications. With a tetra-cationic acceptor-π-acceptor (A-π-A) compound our first success in this field of research was recently reported.[3] The compound was succesfully utilised as a cell imaging agent. Visualisation was possible by two-photon excited fluorescence (TPEF) imaging, due to the well designed two-photon absorption (TPA) and fluorescence properties of the molecule. Good water-solubility, high water-stability, and promising cytotoxicity studies further corroborated the applicability of this compound for live cell imaging. The aim of this work is to improve upon the TPEF performance, i.e. enhancing the quantum yield Φ_f and the TPA cross section σ_2.

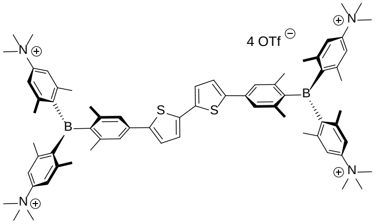

Figure 1. Tetra-cationic, water-soluble compound for TPEF cell imaging.

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The Photophysics of Tolane – A ps time-resolved Photoelectron Imaging Study

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Photoelectron spectra recorded via resonance-enhanced multiphoton ionization (REMPI-PES) contain information on the structure of excited neutral states, since the kinetic energy distribution of the photoelectrons is highly sensitive to the electronic character of the neutral molecule. Time-dependent changes in the spectra thus also yield information on relaxation dynamics after photoexcitation. The combination of small bandwidth ps laser pulses and supersonic jet expansion allows us to excite zero order vibronic states of cold molecules and to elucidate their dynamics.

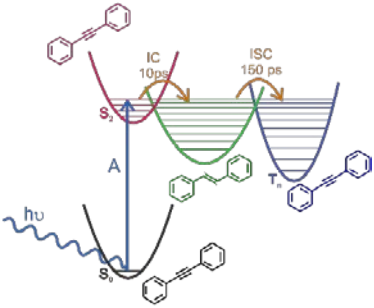

Figure 1. Two-step relaxation model of tolane mediated via a biradicalic trans-bent species.

The subject of our present study is tolane (diphenylacetylene), a fundamental building block in functional organic materials and polymers. The interest on the photophysical properties of tolane is based on the unusual fluorescence behavior. By exciting the vibronic manifold of the first bright excited state, the fluorescence quantum yield rapidly decreases compared to origin excitation.[1] This breakdown is strongly dependent on excitation energy as well as on temperature. Nevertheless, no time-resolved measurements on cold and isolated molecules in the gas phase were carried out so far. In our supersonic jet experiments we were able to determine the lifetimes of different vibronic modes. We found a drop from several ns at the excited state origin to around 10 ps at a vibrational energy of 3000 cm^{-1}. Furthermore tolane relaxes to a long lived triplet state via a two-step sequential relaxation model, probably mediated by a biradicalic *trans-bent* structure showing a lifetime in the 100 ps region.

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Phthalocyanine Star-Mesogens – A Possible Efficient Photovoltaic LC Material?

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Fullerene-filled stilbenoid three-arm stars exhibit an extraordinary self-assembly in LC fullerene triple-helices. [1] Such structures can be obtained from a star mesogen with one C_{60} connected via a spacer or via a 2 : 1 mixture of the parent star with a star containing three fullerenes. In these materials, the oligo(phenylenevinylene) emission is efficiently quenched pointing to a charge separation process. In order to develop this system towards a real photovoltaic material, phthalocyanine is incorporated as a core unit, since they absorb strongly in the red- and infrared and organize in regular π-stacks affording frequently hole conducting columnar LCs.[2] An elaborated and optimised synthetic procedure furnishes star-shaped mesogens **A1**-**A4**. The physical mixing of **A2** with the Fullerene-derivate **A4** (1 : 1) leads to a highly ordered columnar phase consisting of Fullerene quadruple-helices. The driving force is supposed to be nanosegregation and the filling of the intrinsic free space by the fullerenes. [3] In order to further improve the materials properties, we recently replaced the photosensitive stilbenoid arms by oligothiophene units to furnish the stars **B1**-**B4**. Here, we present the synthesis and study of the structure-property relationship of the neat stars and their mixtures with tetra-fullerene substituted derivatives by means of polarized optical microscopy, differential scanning calorimetry, comprehensive X-ray scattering and modeling.

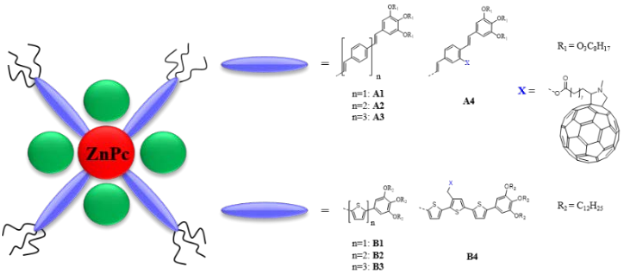

Figure 1: Schematic structure of the star-shaped phthalocyanines ***A1-A4*** *and* ***B1-B4****.*

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[3] M. Dechant, M. Lehmann, unpublished results.

Influence of Architectural Polymer Blends on Bioink Properties for Extrusion-based Bioprinting

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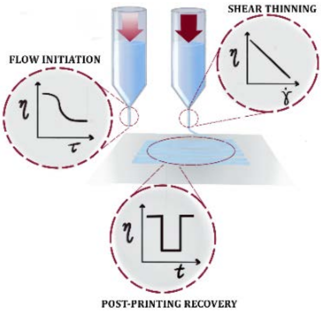

Figure 1. Schematic illustration of rheology measurements used to simulate the extrusion process in bioprinting.

Biofabrication utilizes additive manufacturing methods for the organization of cells into hierarchical constructs. To achieve this, extrusion-based bioprinting uses hydrogels as a printable matrix for cells. However, these bioinks have to meet a host of stringent requirements, resulting in only few suitable systems.

Recently, a diblock copolymer comprising poly(2-methyl-2-oxazoline) (PMeOx) and poly(2-*n*-propyl-2-oxazine) (P*n*PrOzi) was found, forming in aqueous solution a physically crosslinked gel above 20 wt.%. This is based on hydrophobic interactions between P*n*PrOzi blocks as evidenced by small angle neutron scattering.[1] It meets bioink criteria such as non-cytotoxicity, shear thinning behavior and fast post-print recovery.

The dependence of hydrogel properties on P*n*PrOzi block interactions led to the assumption that star-shaped diblock copolymers (SSDC) could act as crosslinking agents, resulting in enhanced mechanical or extrusion properties of the gel. Blends of star-shaped and linear copolymers consisting of P*n*PrOzi and PMeOx were therefore evaluated using rheology. It could be shown that shear thinning and post-print recovery properties of the hydrogel were influenced by the size of the SSDC. Based on this research, tailorable hydrogels can be engineered, extending the library of available systems for the use in biofabrication

[1] T. Lorson, S. Jaksch, M.M. Lübtow, T. Jüngst, J. Groll, T. Lühmann, R. Luxenhofer, *Biomacromolecules* **2017**, *18*, 2161–2171.

Chemistry Meets Cancer Immunotherapy

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Cancer immunotherapy with antibodies and T cells is a rapidly evolving translational research field. Previous work has demonstrated the potential to redirect the specificity of a hapten-antibody h38C2 through chemical programming with peptidomimetics. These peptidomimetics were functionalized by a diketone-group that mediates binding to a reactive lysine residue in the antibody binding site. With this approach, the scope of potential tumor-specific targets can be broadened to comprise antigens that cannot be recognized by conventional antibodies and/or simultaneous targeting of multiple antigens, either concomitantly or sequentially to prevent antigen-escape[1].

The aim of this work is to contribute to the development of chemically programmed antibodies and T cells in cancer immunotherapy. Therefore, different hapten-like compounds have been synthesized which consist of a reactive group, a spacer and either a targeting or labeling module.

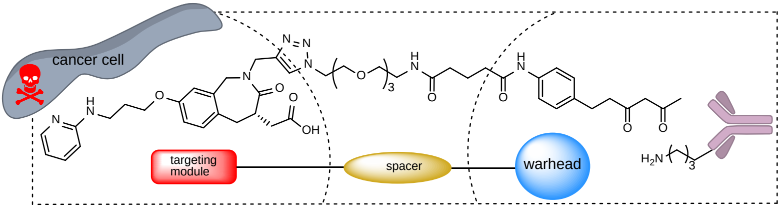

Figure 1 Exemplary and schematic assembly of the desired compounds.

The test results of the molecules, equipped with biotin as labeling module, proofed the concept by showing that the compounds are not binding to reactive groups on the cell surface, but selectively react with the lysine residue of the scFv receptor.

Integrin α(v)β(3), which is overexpressed in solid tumor cells[2], was selected as first target and an Arg-Gly-Asp (RGD)[2] peptidomimetic and a cyclo(RGD)[3] peptide have been synthesized.

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Synthesis of boron containing polycyclic aromatic hydrocarbons via metal-free Hydroboration/C-H-Borylation

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Heteroatom doped polycyclic aromatic hydrocarbons (PAHs) are an important class of organic optoelectronic materials which are widely applied in organic field effect transistors, organic light emitting diodes and organic photovoltaic devices. Whereas nitrogen has primarily been used as “dopant” element due to the large variety of simple synthetic strategies towards N-doped PAHs, the synthesis of boron doped PAHs is rather underexplored. Aiming for new n-type semiconducting materials, we have recently developed a new one-pot synthetic strategy to prepare unprecedented boron-doped perylene derivatives with remarkable stabilities. Thus, boron-doped PAH **4** could be prepared in a tandem metal-free hydroboration/electrophilic C-H borylation using a N-heterocyclic carbene-borenium salt.[1] Doubly boron-doped perylene **4** exhibits visible range absorbance and fluorescence in chloroform solution ($\Phi = 0.63$) and undergoes two reversible one-electron reductions at moderate potentials of −1.30 and −1.64 eV vs. ferrocenium/ferrocene in DMSO. Currently, we are exploring the scope of this methodology and develop larger multiply boron-doped PAHs and nanographene derivatives.

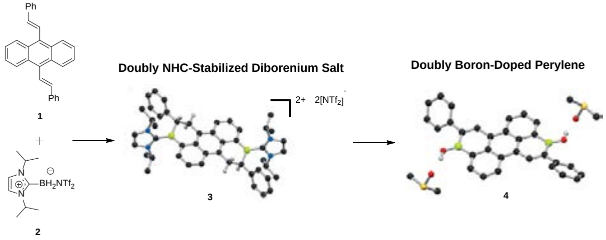

Figure 1. Synthesis of doubly Boron-doped perylene from alkene **1** and NHC-borane **2**.[1]

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Synthesis of anhydrous and aqueous lanthanide cyanoborates

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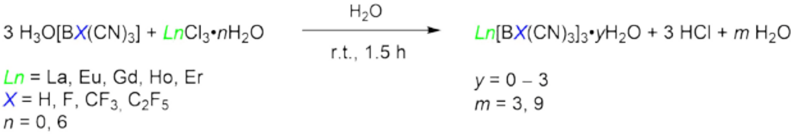
Cyanoborate anions of the type $[BX(CN)_3]^-$ (X = H, F, CF_3, C_2F_5) or the dicyanodihydridoborate anion $[BH_2(CN)_2]^-$ are well known building blocks for metal organic frameworks containing transition metal cations or ionic liquids due to their weakly coordinating properties. So far, only a few examples of cyanoborates containing rare earth metal cations are known.[1] Lanthanide cyanoborates have been synthesized via metathesis starting from the rare earth metal chlorides $LnCl_3{\cdot}nH_2O$ (Ln = La, Eu, Gd, Ho, Er; n = 0, 6) and the respective Brønsted acid $H_3O[BX(CN)_3]$ or $H[BH_2(CN)_2]$.[4]



Scheme 1. Synthesis of cyanoborates containing rare earth metal cations.

The aqueous complexes were dried in a vacuum at elevated temperatures to give the anhydrous complexes which was proven by single crystal X-ray structure analysis and powder X-ray diffraction as well as IR spectroscopy.[2]

Anhydrous complexes of the dicyanodihydridoborate anion $Ln[BH_2(CN)_2]_3$ (Ln = La, Eu, Ho) were dissolved in the corresponding ionic liquid $[EMIm][BH_2(CN)_2]$ (EMIm = ethylmethylimidazolium) and these solutions studied concerning their density, viscosity and conductivity.

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[2] Tatjana Ribbeck, Sven H. Zottnick, Christoph Kerpen, Johannes Landmann, Nikolai V. Ignat'ev, Klaus Müller-Buschbaum, Maik Finze, *Inorg. Chem.* **2017**, *56*, 2278.

Synthetic Routes to Unsymmetric Cationic Triarylborane Chromophores

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Due to the vacant p-orbital of three-coordinate boron, such compounds find application in various fields such as optoelectronics, anion sensors and bioimaging agents.[1] Within the last ca. 30 years, our group has been examining the optical and electronic properties of such systems.

Influenced by the work of Gabbaï and coworkers,[2] we started to synthesize water-soluble triarylboranes such as compound **2** with possible applications in bioimaging.[3] During these investigations, the question arose how many positive charges are required to make the compound soluble in water and allow them to enter cells and stain different organelles therein. Therefore, the synthesis of mono-, di- and tri-cationic compounds was investigated. As control over the exact degree of methylation of the neutral compound **1** was not possible, we started to synthesize compounds **3a-d**.

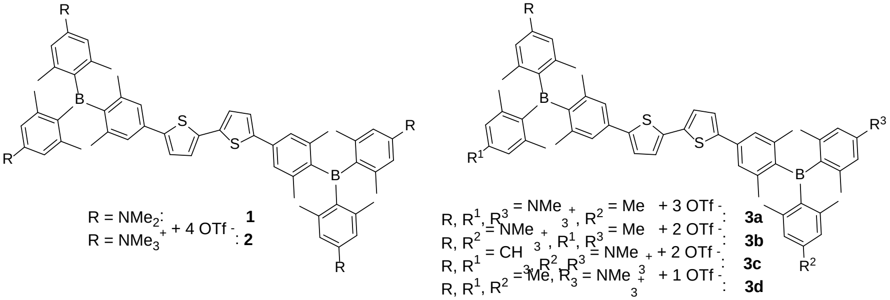

Figure 1: Structures of the neutral compound **1**, the four times cationic compound **2** and the selectively cationic compounds **3a-d**.[3]

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Derivatives of Tribenzotriquinacene for the synthesis of compounds with low lying triplet states

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Biradicals exhibit strong inter radical covalent interactions in an organic radical appears to guarantee metal-like properties.[1] They have been recently synthesized as a new type of semiconductor material for organic devices and have fundamental significance in the fields in mechanistic, synthetic and biological chemistry [2] It has been also expected to have promising applications as functional materials in quantum information processing systems, electronic devices, lithium ion batteries and organic spintronics.[3] Tribenzotriqinacene (TBTQ) is an interesting polycyclic aromatic framework with a particularly rigid, C_{3v} symmetrical, bowl shaped core bearing three mutually fused indane wings. The transformation of TBTQ to tribenzacepentalene by multiple deprotonation creates an aromatic dianion ***(Figure 1)*** and examinations of the singlet and triplet states of the TBTQ core in the dianionic and the neutral state would provide important insights into the features of these molecules has already reported for the parent system [4, 5]. In an attempt to synthesize PAH molecule based on TBTQ core, iodinated tribenzotriquinacenetriol was synthesized and alcohol molecules were protected. In order to properly afford the target molecule the protected molecules will be deprotected and then removed following the annulation reaction.

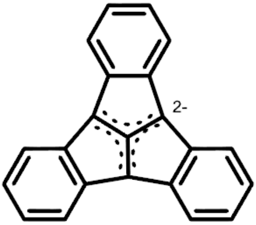

Figure 1 Dianion structure of TBTQ by multiple deprotonation

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A large Stokes shift fluorogen-activating RNA aptamer

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Large Stokes shift (LSS) fluorescent proteins (FPs) exploit excited state proton transfer pathways to enable fluorescence emission from the phenolate intermediate of their internal 4 hydroxybenzylidene imidazolone (HBI) chromophore.[1]

Here, we report an RNA aptamer named Chili that mimics LSS FPs by inducing highly Stokes-shifted emission from several green and red HBI analogs that are non-fluorescent when free in solution. The ligands are bound by the RNA in their protonated phenol form and feature a cationic aromatic side chain for increased RNA affinity and reduced magnesium dependence.

In combination with oxidative functionalization at the C2 position of the imidazolone, this strategy yielded DMHBO^+, which binds to the Chili aptamer with a low-nanomolar K_D.

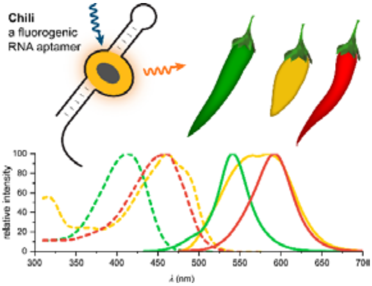

Figure 1. Fluorogenic dyes with a broad variety of emission maxima are activated by the Chili aptamer. Stokes shifts of around 150 nm are achieved.

Because of its highly red-shifted fluorescence emission at 592 nm, the Chili–DMHBO^+ complex is an ideal fluorescence donor for Förster resonance energy transfer (FRET) to the rhodamine dye Atto 590 and will therefore find applications in FRET-based analytical RNA systems.[2]

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Ein wasserlösliches Perylenbisimid-Cyclophan für die Erkennung aromatischer Alkaloide

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Seit C. J. Pedersons Entdeckung der Kronenether im Jahr 1967[1] sind Forscher von makrozyklischen Molekülen und deren Eigenschaft, Gäste in ihrem Innern zu binden, fasziniert.[2]

Basierend auf der Struktur eines zuvor in unserer Gruppe untersuchten *para*-Xylylen-verbrückten Perylenbisimid (PBI)-Cyclophans, dass als Fluoreszenz-*turn-on*/*turn-off*-Sensor für polyzyklische Kohlenwasserstoffe in $CHCl_3$ agiert,[3] wurde der wasserlösliche Wirt **[2PBI]-1** (Abbildung 1) entworfen. Dieser neue künstliche Rezeptor bindet verschiedene aromatische Alkaloide wie Harmin (**G1**) in wässriger Umgebung, was sich in deutlichen Änderungen der UV-Vis- und Fluoreszenzeigenschaften des Chromophor-Wirts bei Gasteinlagerung zeigt. Die Struktur des gebildeten Komlexes **G1⊂[2PBI]-1** konnte mittels 2D-NMR-Spektroskopie aufgeklärt werden. Derzeit fokussieren wir uns auf die Erforschung weiterer Bindungseigenschaften von **[2PBI]-1** und auf die Entwicklung einer Struktur-Bindungsaffinitäts-Beziehung für verschiedene Alkaloid-Gäste.

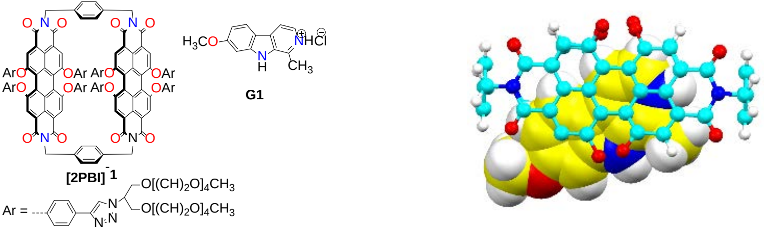

Abbildung 1. Molekülstrukturen vom Rezeptor **[2PBI]-1** und dem Alkaloid **G1** und berechnete Struktur (PM7) des Komplexes **G1⊂[2PBI]-1** (aus Gründen der Übersichtlichkeit sind die Arylreste ausgeblendet).

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Self-assembly in Water

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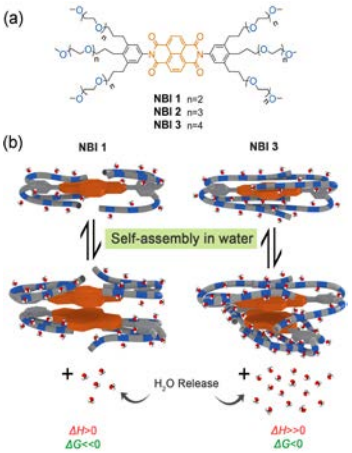

Figure 1. (a) Chemical structure of NBI 1-3. (b) Schematic illustration of self-assembly of NBI 1 and NBI 3 and corresponding changes in thermodynamic parameters.

Water plays a pivotal role in all life-forms in directing the formation of different nano and mesoscale structures like amyloid fibrils, actin filaments etc. The major non-covalent interactions that drive self-assembly in water are H-bonding and hydrophobic interactions. Water orients it's H-bonds differently around particles of different sizes. For small systems (<1nm), this arrangement leads to an unfavorable entropy (due to lesser degrees of freedom around the solute) and for larger systems (<1nm), this leads to an unfavorable enthalpy (due to the breakage of H-bonds). Non-polar molecules self-assemble in water to compensate this entropic or enthalpic penalty [1].

In this work, self-assembly studies of several conjugated dyes in aqueous media were presented. On one hand, thorough investigations of the thermodynamics of self-assembly in water were carried out. On the other hand, self-assembly behaviors and biological application of the squaraine dyes [2].

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Machine Learning Based Patchy Particle Model for Simulating Self-Assembly of Zn Chlorin

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Patchy particle is a promising model to study long-time behaviour of molecular aggregates efficiently with substantial accuracy.[1] It reduces the computational cost to analyse a complex molecule by approximating it to an imaginary particle system which considers the significant long-range potentials and ignores the insignificant contributions. This work focuses on the study of supramolecular properties of zinc chlorin molecules and development of parameters for the patchy particle system that could mimic aggregation of the zinc chlorin. Semisynthetic zinc chlorin sounds a promising candidate for the development of opto-electronics devices with structural and functional properties as those of light harvesting complex. This light harvesting system has the exceptional property of being self assembled without the support of any protein matrix. Simple synthesis, better chemical stability and nearly same spectral blueprints to naturally occuring counterparts, strengthen its candidacy for opto-electronic applications. But its poor solubility increase the likelihood of precipitations that causes difficulties in reaching the desired structural properties. The self-assembly is driven by non-covalent interaction only such as π-stacking, hydrogen bonding and metal oxygen coordination that leads to formation of tubular liquid crystalline structures that perform energy and charge transfer.[2] We propose a method of employing a machine learning based approach, where a high resolution potential energy distribution map (considering all the 6 degrees of freedom, which is derived from DFTB), is used as training dataset to find out the necessary parameters of the approximate patchy particle system.

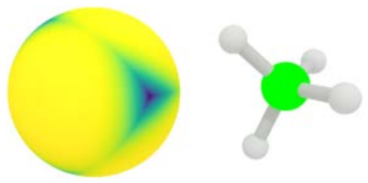

Figure 1: Interaction potential map of the patchy particle. Dark blue corresponds to the attractive patch

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Spectroscopic properties of divalent Samarium

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The spectroscopic properties of compounds containing trivalent and divalent lanthanides have been investigated during the recent past decades. In compounds containing trivalent lanthanide ions the luminescence is based on parity forbidden f-f-transitions. Since the 4f-states are well shielded and possess core-close probability regions, the energetic states of the 4f-levels are not influenced by ligands, which leads to sharp emission-bands.[1]

For divalent lanthanide species, the spectroscopic properties change dramatically and provide parity allowed charge transfer from 4f into 5d-states and *vice versa.* The population of 5d-states also brings non-shielded states into play, which are influenced by chemical surroundings leading usually into broad band excitation and emission bands.[2]

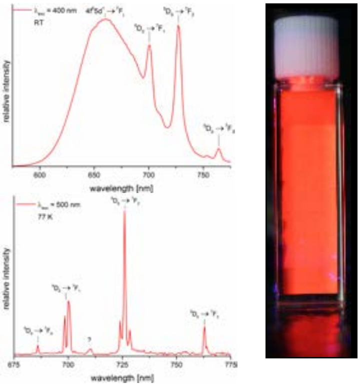

Figure 1. Top: Emission spectrum of Sm^{2+} at RT; Bottom: Emission spectrum of Sm^{2+} at 77K.

For a few examples of divalent Samarium species, the chemical surrounding leads to a slightly lower relative energy of the $4f^6$ excited states in comparison to $4f^55d^1$ excited states, which enables a thermal population of the $4f^55d^1$ excited states. This means, at increased temperatures, the $4f^55d^1 \rightarrow 4f^6$ broad band emission can be observed whereas at low temperatures sharp lines of the $4f^6 \rightarrow 4f^6$ transition will more likely be observed.[3] Since now, this behavior is only reported for Sm^{2+} doped in different host lattices.[4, 5] In our work, we investigate Sm^{2+}-salts providing this feature.

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Regioselective Functionalization of [60]Fullerene Utilizing a Covalent Organic Cage Compound as a Supramolecular Shadow Mask

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[60]Fullerene and its multiple exohedral adducts are attractive materials for applications in medicinal chemistry and material sciences due to their unprecedented structural and electronic properties.[1] The synthesis of specific regioisomers for C_{60} derivatives is however indispensably associated with time consuming synthetic protocols, tedious preparative HPLC separations and typically low yields.[2] Significant improvements have been achieved by employing tether-directed remote functionalization approaches.[3] However, these methods still suffer from elaborate tether synthesis and difficulties in postsynthetic modifications.

Here we report on the size-specific encapsulation of fullerenes C_{60} and C_{70} within a trigonal-bipyramidal organic cage[4,5,6] and the utilization of these host-guest complexes as supramolecular shadow masks for the regioselective functionalization of C_{60} with untethered malonate derivatives.[7]

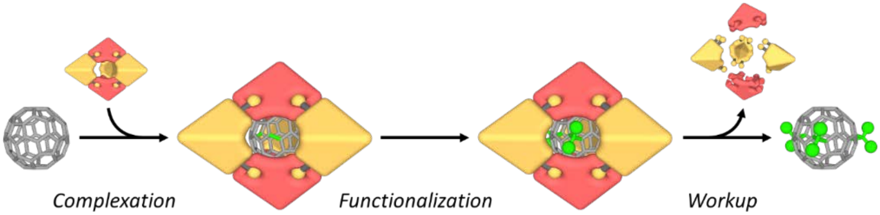

Figure 1. A Supramolecular “Shadow Mask” for the Regioselective Functionalization of C_{60}.

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Photocatalytic hydrogen evolution using a ruthenium terpyridine complex as photosensitizer

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Terpyridines (2,2‘:6‘,2‘‘-terpyridines) have a high affinity to coordinate to many metal ions and the resulting complexes are found in a broad field of applications.[1] One application is the photoreduction of water to form hydrogen as a usable fuel by mimicking natural photosynthesis. Such a system for artificial photosynthesis is composed of two main components. The electrocatalyst catalyzes the reduction of water. The photosensitizer absorbs light and transfers the energy via electron transfer to the electrocatalyst.[2] In order to do so, coordination to the electrocatalyst and thus intramolecular electron transfer can overcome the barriers of diffusion (see Figure 1). Therefore, a ligand with peripheral pyridine rings as additional coordination sites is synthesized and used for the complexation with ruthenium. The photophysical and electrochemical properties of this complex are investigated and its ability to act as a photosensitizer is tested in an artificial photosynthesis system. A previously unreported activity as photosensitizer of ruthenium terpyridine complexes and consequential a stable hydrogen evolution over more than ten days is observed.[3]

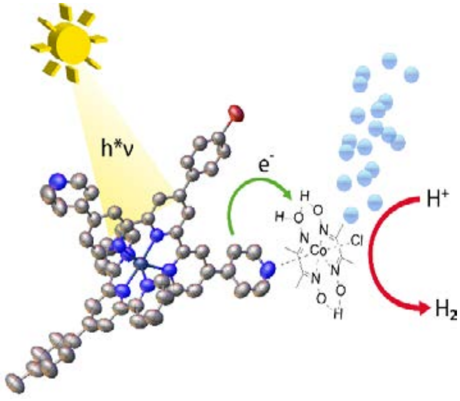

Figure 1. Schematic representation of the hydrogen evolution by a system composed of a ruthenium terpyridine complex as photosensitizer and cobaloxime as electrocatalyst.

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Alkali Metal Aminotroponiminates: Coordination, Redox Chemistry and Reactivity

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Aminotroponiminates (ATIs, Fig. 1, top) are a well-established class of ligands and have been used for complexation of (semi-) metals across large sections of the periodic table.[1]

We turned our attention to alkali metal ATIs. In the course of these studies, it has been demonstrated that the ATI ligand backbone can act as a binding site, leading to an unexpectedly rich coordination chemistry of this ligand set.[2] Moreover, ATIs undergo unusual ligand induced disproportionation reactions.[3]

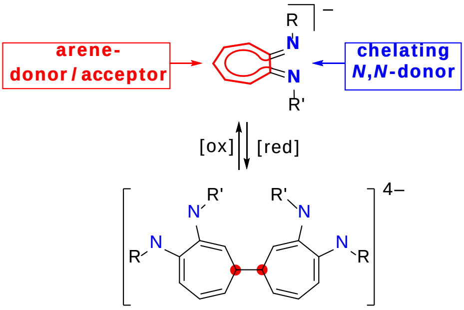

Figure 1. Binding sites of ATIs and reductive dimerization and oxidative monomerization of alkali metal ATIs.

In electrochemical studies we have shown that ATIs can act as redox-active ligands. Under strongly reducing conditions, alkali metal ATIs undergo highly selective and chemically reversible C–C coupling reactions.[4] The regio- and diasteroselectivity of the dimerization can be controlled by choice of the metal in the *N,N*-binding pocket, the substituents at the nitrogen atom and the solvent.

Neutral monometallic and the first examples of ionic homo- and heterobimetallic alkali metal ATIs show excellent properties as initiators in the ring opening polymerization of ε-caprolactone.[3]

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Ancistrolikokine E_3, a new naphthylisoquinoline alkaloid with potent activity against pancreatic cancer cells

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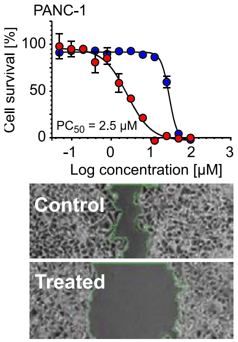
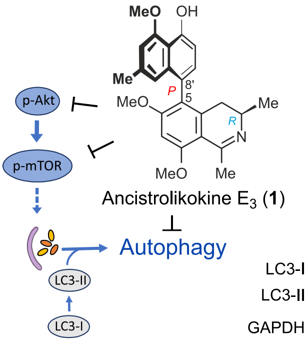
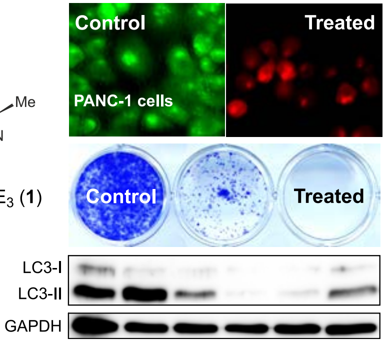
Pancreatic cancer is one of the deadliest forms of cancers, killing 95% of patients within 5 years. PANC-1 human pancreatic cancer cells are characterized by their ability to maintain sustained and continuous proliferation even under extreme conditions of nutrient and oxygen deficiency. This phenomenon is termed as “austerity”.[1,2]

Ancistrolikokine E_3 (**1**),[3] a new naphthyldihydroisoquinoline alkaloid discovered in the Congolese liana *Ancistrocladus likoko*, was found to exert a potent preferential cytotoxicity on PANC-1 cancer cells *in vitro* with a PC_{50} value of 2.5 µM. Mechanistic studies on **1** revealed that the compound inhibits cancer cell mobility, induces morphological alterations leading to complete cancer cell death, and prevents PANC-1 cell migration and colonization and, thus, metastasis formation. This study provides the first live evidence of the effect of a naphthyldihydroisoquinoline alkaloid on PANC-1 cancer cells and shows that the cell death induced by compound **1** proceeds mainly through the inhibition of the Akt/mTOR pathway. Additionally, the compound is considered to be a potent early-stage inhibitor of the autophagy pathway (intracellular self-degradative process), as it strongly affects its key regulators, Atg5, Atg12, Beclin-1, LC3-I, and LC3-II. This study shows that compound **1** might be a promising lead compound for the development of new agents against pancreatic cancer.







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[2] K. Kato et al., *Oncogene* **2002**, *21*, 6082.
[3] S. Awale et al., *J. Nat. Prod.* **2018**, *81*, 2282.

Novel naphthylisoquinoline dimers, from a Congolese *Ancistrocladus* plant, with antiprotozoal activities

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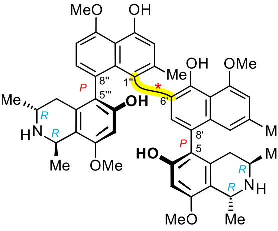
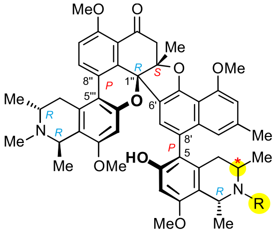
Naphthylisoquinoline alkaloids[1] are the only known isoquinoline natural products of polyketidic origin. They display unique molecular scaffolds, consisting of a naphthalene and an isoquinoline moiety connected by a (usually) rotationally hindered *C*,*C*- or *N*,*C*-axis. They also exist as dimers, which show most fascinating stereochemical peculiarities, with up to three consecutive chiral biaryl axes. Depending on their individual structures, some of them exhibit promising antiprotozoal, antiviral, or antitumoral activities.[1]

From the leaves of a botanically as yet undescribed *Ancistrocladus* species endemic to the rainforests near the Congolese town of Mbandaka, a series of novel-type dimeric naphthylisoquinoline alkaloids have been discovered recently:

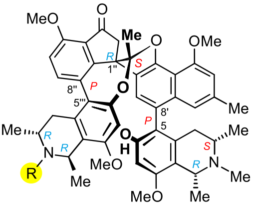
- the mbandakamines A (**1a**) and B (**1b**), the first dimers with a constitutionally highly unsymmetric 6′,1″-linked central biaryl axis,[2,3]
- the cyclombandakamines A₁ (**2**) and A₂ (**3**), the first dimers with oxygen bridges,[4] and
- the spirombandakamines A₁ (**4**) and A₂ (**5**), the first naphthylisoquinoline dimers with spiro-fused molecular frameworks.[5]



1a: *P* at the central axis
1b: *M* at the central axis



2: R = H, *R* at C-3
3: R = Me, *S* at C-3



4: R = H
5: R = Me

Our poster reports on the LC-UV-MS-CD-assisted isolation and structural elucidation of these thrilling dimers, and on their antiprotozoal activities. Moreover, we provide a plausible biosynthetic origin of these unprecedented quateraryls.

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Synthesis of the antiplasmodial and antileukemic naphthylisoquinoline alkaloids dioncophylline C, dioncophylline F, and 5'-*O*-methyldioncophylline D

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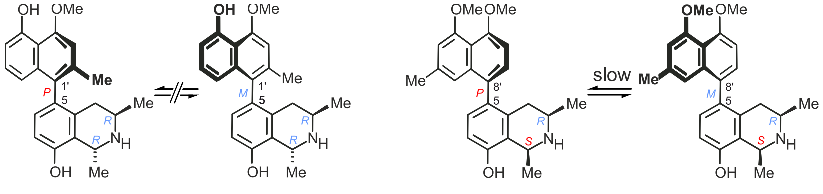
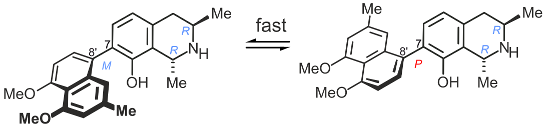
The total synthesis of naphthylisoquinoline alkaloids is a highly rewarding - and yet challenging - task. These natural products possess both, stereogenic centers and chiral axes. The steric hindrance at these axes may differ drastically: Thus, in dioncophylline C (**1a**), the axis is rotationally hindered giving rise to a stable stereogenic element, while the atropo-diastereomers of dioncophylline F (**2**), i.e. **2a** and **2b**, interconvert slowly and those of 5'-*O*-methyldionophylline D (**3**), i.e. **3a** and **3b**, even rapidly.

Here we describe the total synthesis of **1a**, **2**, and **3** by a non-diastereoselective Suzuki-Miyaura coupling as the crucial, biaryl-bond forming step. While in **1a** and **1b** the configuration at the axes is stable and each of the atropisomers is obtained in a stereochemically pure form by HPLC resolution, the synthesis of **2a/b** and **3a/b** yields the equilibrium mixtures of the interconverting atropisomers.



1a **1b** **2a** **2b**



3a **3b**

In the case of the highly antimalarial dioncophylline C (**1a**), current synthetic work is directed towards the preparation of structurally related analogs for structure-activity relationship studies. For the elucidation of the mode of action of the antileukemic 5'-*O*-methyldioncophylline D (**3**), we managed to synthesize an analog equipped with a biotin probe.

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Manufacturing electrodes in an infiltration process with high temperature modifications of detonation diamonds

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Detonation diamonds are well known for their high specific surface, therefore they were selected as a precursor material for high temperature annealing.[1] The process temperature was selected above the Debye temperature of diamonds to obtain excitation of all the vibrational states. Transmission electron microscopy (TEM) was the tool of choice to investigate the carbon modifications which arose during this high-temperature treatment. The annealed sample included polyhedral and onion like particles as well as areas of few-layered graphene ribbons. The presence of few-layered graphene ribbons additionally increases the electrical conductivity.[2] A stable dispersion of these particles was achieved by deagglomerating the particles with an attrition mill and with the aid of surfactants. This dispersion was used as starting material for electrodes manufactured by an infiltration process.

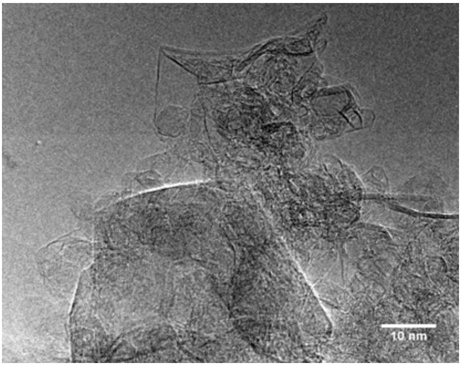

Figure 1. TEM image of the annealed diamond.

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Stable Isoindigo Radicals and Biradicals: Synthesis, Isolation and Characterization

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Open shell organic molecules are of fundamental interest for organic magnetism and spintronics, singlet-fission and energy storage but their inherent instability often leads to (fast) degradation.[1] One strategy to stabilize them are (electron deficient) quinoidal frameworks that are in resonance with singlet biradical structures.[2] In this contribution, we report the first examples of isoindigo radicals and biradicals with remarkable stabilities, facilitating their unambiguous characterization with min. $\tau_{1/2}$ up to 28 d for biradical OS-2$^{\cdot\cdot}$. According to our detailed experimental and computational studies, the biradicaloid isoindigo derivative exhibits a singlet-open shell ground state, with a small ΔE_{ST} of 65 meV. Therefore, temperature dependent magnetic properties could be elaborated for this unprecedented biradicaloid system by NMR and EPR spectroscopic techniques. [Fig. 1].

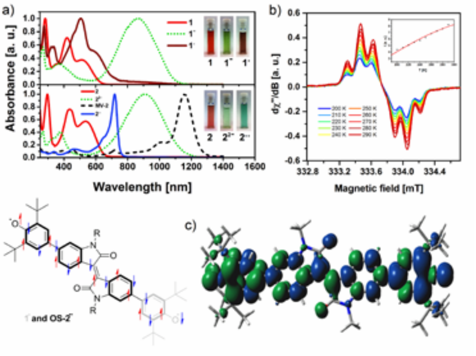

Figure 1. (a) UV/Vis absorption and (b) temp. dependent EPR-spectra of **OS-2**$^{-}$ (c) electron density distribution of **OS-2**$^{-}$

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Synthesis and Characterization of Drug Loaded Silica Gel Fibers

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[1] Translational Center Regenerative Therapies, Fraunhofer ISC, Neunerplatz 2, Würzburg, Germany.
[2] Functional Polymer Materials, Chair for Advanced Materials Synthesis, Department Chemistry and Pharmacy, Julius-Maximilians-University Würzburg, Röntgenring 11, Würzburg, Germany.
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Synthetic organic-inorganic hybrid biomaterials are in focus of biomaterials research since many years and already entered the marked as medical products.[1] These materials combine synergetically the advantages of organic and inorganic devices.

One example are sol-gel derived bioresorbable silica gel microfibers[2], whereof one fiber formulation is CE-approved for the regeneration of diabetic ulcer and 2nd degree burning wounds (figure 1). The nanostructured surface of the fibers enhances the directed movement of cells[3] and the release of ortho-silicic acid while fiber degradation results in an anti-inflammatory wound healing[4], which opens up new perspectives in therapies as a smart bioactive implant.

Figure 1: Picture of a CE-approved silica gel fiber fleece. © K. Dobberke, Fraunhofer ISC.

In this study these silica gel fibers are further developed into a carrier of drugs. Here, polyoxazoline block copolymers were loaded with a hydrophobic model drug[5], dispersed into silica gel sols and finally spun to endless microfibers. After characterization of the obtained fibers degradation studies and drug release profiles were performed under physiological conditions.

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Photoluminescence microscopy of low-dimensional nanoscale heterojunctions

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Heterojunctions are an essential component in a variety of modern semiconductor devices. Recent research has focused on a novel type of heterojunction formed at the interface between two-dimensional materials like graphene, MoS_2 and $WoSe_2$.[1] These structures are found to give rise to so called interlayer excitons, in which bound electrons and holes are localized in different layers. Such interlayer excitons display remarkable properties like extraordinarily long fluorescence lifetimes in the nanosecond regime, about an order of magnitude longer intralayer excitons of the parent materials.[2]

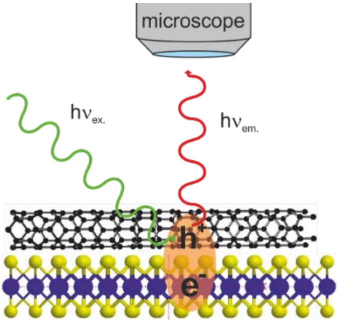

Figure 1: Schematic illustration of the PL microscopy experiment. A laser optically generates interlayer excitons. The resulting emission from their decay enters a microscope objective, is detected, and analyzed using a spectrometer.

Here we plan to investigate heterojunctions between low-dimensional materials such as nanotubes and two-dimensional, atomically thin semiconductors. The preparation of suitable samples and the difficulty of probing photophysical phenomena at the nanoscale make the design of such experiments challenging. The proposed research will focus on the fabrication and investigation of heterojunctions between semiconducting carbon nanotubes or perowskite nanoplatelets and 2D-semiconductors such as MoS_2. The emission properties of these systems will be investigated using a combination of photoluminescence microscopy and time-resolved photoluminescence. We hope that such experiments will also yield new insights into the interactions between different low-dimensional semiconductors. Advances in the field of nanoscale heterojunctions may also pave the way for the design of new light emitting diodes, lasers or photovoltaic devices, using nanoelectronic structures.

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Stereoelectronic Properties of *N*-Heterocyclic Silylenes

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Knowledge of the steric and electronic properties of a ligand can be vital for the design of catalysts and for understanding reaction patterns. These properties have been widely examined for several groups of ligands such as phosphines and *N*-heterocyclic carbenes.[1]

To determine the σ-donor strength of a ligand the *Tolman Electronic Parameter* (TEP) can be utilized, which is based on the measurement of the A_1 C–O vibrational mode of complexes like $[Ni(CO)_3L]$.[2] Another way to assess the σ-donor strength is the measurement of $^1J_{W\text{-}C}$ coupling constants in ^{13}C NMR spectroscopy of tungsten complexes.[3] Insight into the steric bulk of the ligand can be gained by analyzing the *percent buried volume (*$\%V_{bur}$*)* which is determined by using X-ray crystallographic data.[4] By this, statements about the space occupied by the ligand in the first coordination sphere of the metal center can be made.

Herein, we wish to report first results of the investigation of the steric and electronic properties of the *N*-heterocyclic silylene 1,3-bis(2,6-di*iso*propylphenyl)-1,3-diaza-2-silycyclopent-4-en ($Dipp_2NHSi$) and a comparison to those of common *N*-heterocyclic carbenes.

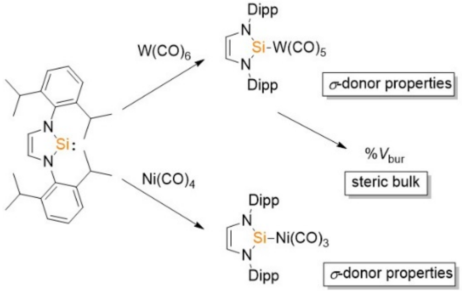

Figure 1. Reaction pathways of silylene $Dipp_2NHSi$ with $W(CO)_6$ and $Ni(CO)_4$ for investigation of electronic and steric properties.

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Nanoparticles for *In-vitro* and *In-vivo* Applications

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The main emphasis of the competence team Theranostics at the Fraunhofer Translational Center Würzburg for Regenerative Therapies on products enabling highly efficient and personalized therapy accompanying in vitro and in vivo diagnosis or even combine diagnosis and therapy in situ.

Well-tailored multifunctional nanoparticles (NPs), which are in focus of our R&D work, are playing a major role in the development of future oriented advanced functional materials for life science applications e.g. contrast agents in medical imaging, *in-vitro* and *in-vivo* diagnostics, drug delivery as well as tissue engineering. Especially, inorganic-organic biohybrid NPs are considered to be important for the development of smart materials and novel technologies for medical applications.

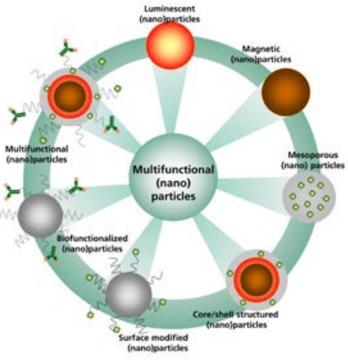

Figure 1. Various (nano)particle systems at Fraunhofer ISC.

NPs can be prepared by wet-chemical methods: sol-gel, precipitation or hydrothermal synthesis. The main focus of our R&D work on inorganic and hybrid materials e.g. silicate based materials, calcium fluoride and phosphate, TiO_2 and iron oxide. To ensure multifunctionalty different approaches can be applied e.g. labelling of NP matrix with organic dyes or lanthanoid ions as well as combination of various materials by core-shell NP design. The resulting NPs are subsequently modified with various chemical functionalities and biological moieties using conventional functionalization and bioconjugation methods. They great potential of new developed NPs as immunodetection assay labels, contrast agent for medical imaging or tool for tumor therapy is demonstrated by the different projects.

Pyrene MO Shuffle

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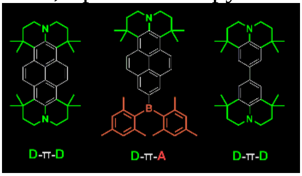
Pyrene is a polycyclic aromatic hydrocarbon (PAH) that has unique photophysical properties which make it suitable for a broad range of applications.[1] The 2,7-positions of pyrene are situated on nodal planes in both the HOMO and LUMO, hence electrophilic reactions take place at the 1-, 3-, 6-, and 8-positions. We developed a selective method to substitute directly the 2,7-positions by an iridium-catalyzed C-H borylation.[2] We report a series of novel pyrene derivatives substituted at the 2- and 2,7-positions with a julolidine-type moiety as a very strong π donor, giving D-π and D-π-D systems, and with Bmes$_2$ as a very strong π acceptor leading to a D-π-A system. These compounds exhibit unusual photophysical properties such as emission in the green region of the electromagnetic spectrum in hexane, whereas all other previously reported pyrene derivatives substituted at the 2,7-positions show blue luminescence. Furthermore, spectroelectrochemical measurements suggest an unexpectedly strong coupling between the substituents at the 2,7-positions of pyrene in the D-π-D system. Theoretical studies show that these properties result from the very strong julolidine-type donor and Bmes$_2$ acceptor coupling efficiently to the pyrene HOMO-1 and LUMO+1, respectively. Destabilization of the former and stabilization of the latter lead to an orbital shuffle between HOMO and HOMO-1, and LUMO and LUMO+1 of pyrene. Consequently, the S$_1$ state changes its nature sufficiently to gain higher oscillator strength. The photophysical and electrochemical properties are thus greatly influenced by the substituents.[3]



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Drug-Polymer Interactions in Paclitaxel-Loaded Micelles

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During the last decades, the scarce natural product paclitaxel with its complex molecular architecture, became one of the market-leading anti-cancer drugs. It developed into the most successful drug against ovarian and breast cancers, yet the overall activity is hampered by its poor solubility.(1)

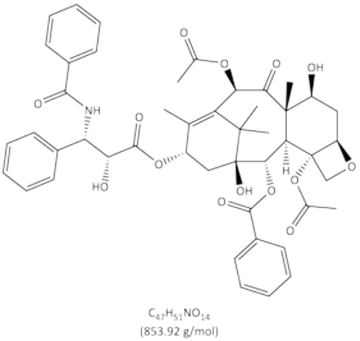

Figure 1. Molecular structure of Paclitaxel

One possibility to overcome this solubility issue is the use of micelles as means of transport.(2) We investigate these micellar formulations using solid-state NMR. So far, we could clearly distinguish between paclitaxel and the block co-polymer poly(2-oxazoline), as well as their corresponding physical mixture and formulations at different drug-polymer ratios. Based on these first results, we started to investigate the drug-drug and drug-polymer interactions. With the help of these characteristic interactions, we want to gain information on the orientation and packing of the drug molecules inside the micelles. Temperature dependent measurements additionally help to distinguish different mobile parts. CASTEP/GIPAW(3) calculations complement these structural elucidations.

The identification of specific drug-polymer interactions will be a step towards a better understanding of this specific structural formulation with the possibility to translate the finding to other drug-polymer systems.

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Self-Sorting and Functionalization of Covalent Organic Cage Compounds

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Porous functional materials have recently gained increased interest in materials sciences regarding potential applications in heterogeneous catalysis, sensing, gas storage and separation, or membranes.[1, 2] In particular, covalent organic cage compounds as discrete molecular objects combine unique properties such as solution processability with intrinsic porosity. Efficient cage synthesis can be achieved through dynamic bond formation in boronate esters or imines.[3]

Here we report on the synthesis of a series of covalent organic cage compounds based on catechol-functionalized tribenzotriquinacene (TBTQ) derivatives and various diboronic acids. Following a molecular design approach, geometrical shapes, structures and sizes of these molecular nanoarchitectures can be adjusted by controlling the bite angles of the respective building blocks.[4, 5] Through the implementation of modified precursors,[6] functionalized cages can be obtained with high spatial precision. Furthermore, multi-component reaction mixtures lead to competitive, narcissistic or social self-sorting processes and cage-to-cage transformations can be performed reflecting the relative stabilities of these cages.

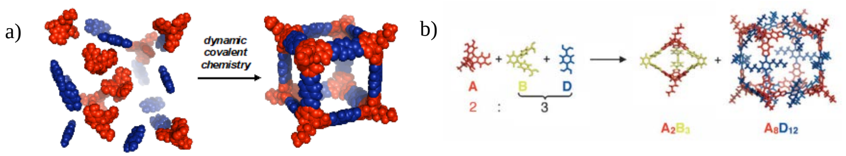

Figure 1. a) Covalent organic cage formation via dynamic covalent chemistry. b) Narcissistic self-sorting.

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In-situ nitrile trimerization as key step for the formation of Sb/Bi-based coordination polymers

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Small aromatic nitrile compounds, such as 1,3,5-tricyanobenzene, are well known starting materials for the synthesis of covalent organic frameworks (COFs). In these reactions the trimerization of the nitrile groups that leads to the formation of a polymeric structure is promoted by the presence of Lewis acids, such as $ZnCl_2$.[1]

In contrast, the addition of Sb^{3+}- or Bi^{3+}-halides instead of the usually used Lewis acids leads to a controlled single trimerization of the aromatic nitrile molecules resulting in the formation of triple functionalised triazine ligands.[2] Subsequently, these *in-situ* generated ligands serve as organic linkers for the formation of Sb/Bi-based coordination polymers (CPs) featuring big conjugated π-systems.

By usage of the aromatic nitriles 1,4-dicyanobenzene and 4-cyanopyridine as organic reagents a variety of Sb/Bi-CPs, such as ${}^{3}_{\infty}[Bi_2Br_6(4\text{-tcpt})]$,[2] (4-tcpt: 2,4,6-tris(4-cyanobenzene)triazine) can be obtained. Their conjugated π-systems can participate in photoluminescence processes[3] resulting in extraordinary properties, such as excitation dependent emission or luminescence at higher temperatures in comparison to other Sb/Bi-CPs with smaller aromatic linkers.[2-4]

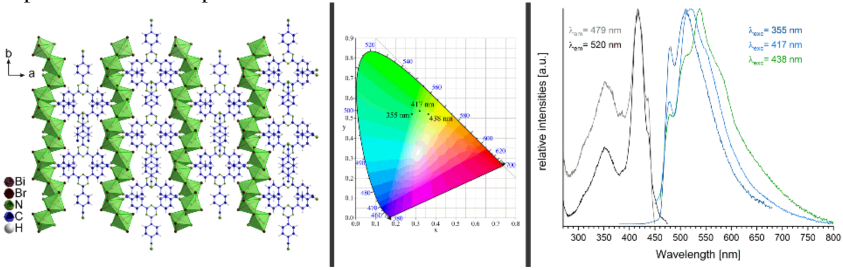

Figure 1. ${}^{3}_{\infty}[Bi_2Br_6(4\text{-tcpt})]$: Excerpt of the crystal structure (left), CIE diagram visualising the excitation dependent emission (middle, λ_{exc} are given in the diagram), excitation and emission spectra (right, 77 K).[2]

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Undecahalogenierte 1-Amino-carba-*closo*-dodecaborat-Anionen

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In unserem Arbeitskreis wurden Cluster-Aufbaureaktionen zu perhalogenierten Carba-*closo*-dodecaborat-Anionen mit einer Aminogruppe entwickelt. Ein Beispiel ist die regioselektive Umsetzung des [3-NC-*closo*-$B_{11}F_{10}$]$^{2-}$-Anions[1] mit Trimethylsilylcyanid zu [1-(Me_3Si)N-2-NC-*closo*-1-$CB_{11}F_{10}$]$^{2-}$ und dessen nachfolgende Umwandlung zu [1-H_2N-2-NC-*closo*-1-$CB_{11}F_{10}$]$^{-}$.

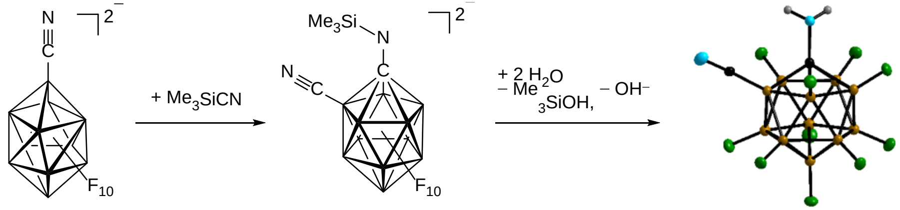

Abbildung 1: Synthese des [1-H_2N-2-NC-*closo*-1-$CB_{11}F_{10}$]$^{2-}$-Dianions.

Analoge Reaktionen wurden auch ausgehend von Salzen der *closo*-Undecaborat-Anionen [*closo*-$B_{11}X_{11}$]$^{2-}$ (X = Cl, Br) ausgearbeitet. Vor allem Salze mit dem [1-H_2N-*closo*-1-$CB_{11}Cl_{11}$]$^{-}$-Anion sind nunmehr besonders einfach zugänglich und erste Studien zu deren Eigenschaften wurden durchgeführt.

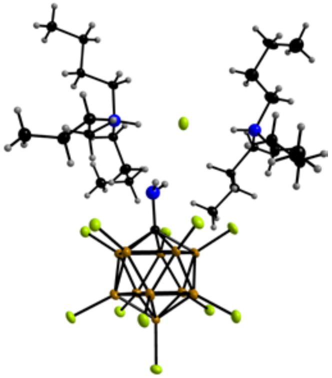

Abbildung 2: Bindungsmotiv im [NEt_3H]$^{+}$- und [NBu_3H]$^{+}$-Salz des [1-H_2N-*closo*-1-$CB_{11}Cl_{11}$]$^{-}$-Anions.

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Kinetics of functionalization reactions of carbon nanotubes

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Impurities in semiconductors often play a key role for enabling device functionality, for example by acting as donors or acceptors for semiconductor doping or by modifying photophysical properties in beneficial ways. Specifically, the introduction of near infrared emissive defect states in covalently functionalized semiconducting single-wall carbon nanotubes (s-SWNTs) has led to the realization of single photon sources at room-temperature and at telecom wavelengths.[1]

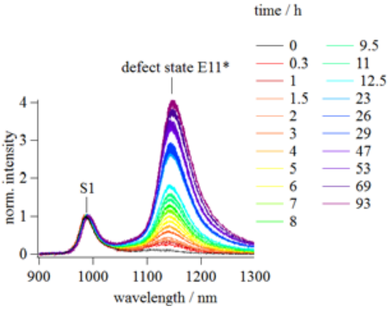

Figure 1. Time-dependent photoluminescence of a functionalized s-SWNT suspension by arylation.

However, the mechanisms underlying such functionalization are not yet well understood.

To further elucidate the reaction mechanisms we have thus investigated the kinetics of s-SWNT functionalization by arylation and reductive alkylation on a timescale from seconds to days using absorption and photoluminescence (PL) spectroscopy (see Fig.1).

Experiments suggest that the arylation proceeds via a two-step mechanism occurring on two different time-scales. For the reductive alkylation we find a complex following reaction. Moreover, we identify the reductive alkylation to be photo-stimulated which may allow a controlled functionalization of s-SWNT based light emitting diodes for photonic applications.

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Chlorocyanoborate Anions: Synthesis, Salts, and Ionic Liquids

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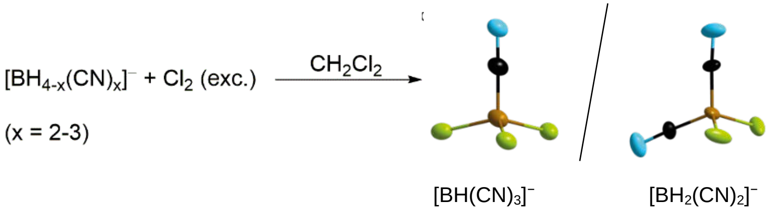
Mixed cyanohydridoborate anions $[BH_{4-x}(CN)_x]^-$ (x = 1–3) are valuable building blocks for low-viscosity room temperature ILs.[1,2,3] However, these ILs show a limited electrochemical stability.[1] The successive substitution of cyano groups in $[B(CN)_4]^-$ by fluorine leads to a significant decrease in viscosity and increase in specific conductivity of ILs based on the anions $[BF_{4-x}(CN)_x]^-$ (x = 1–3) similar to the aforementioned cyanohydridoborate ILs. The comparison of the so far unknown chlorocyanoborate ILs to the previously studied cyanofluoro- and cyanohydridoborate ILs is of general interest with respect to the influence of mass and symmetry of the borate anion on the properties of the ILs. Salts of the anion $[BCl(CN)_3]^-$ were formed during the preparation of $[BF(CN)_3]^-$ from $[BH(CN)_3]^-$[4] and $[B_2(CN)_6]^{2-}$ from $B(CN)_3^{2-}$.[5,6] Here, we report on the synthesis and properties of the isolated and extensivly characterized $[EMIm]^+$, $[BMPL]^+$ and $[Ph_4P]^+$ salts and ILs of these mixed chlorocyanoborate anions $[BCl_{4-x}(CN)_x]^-$ (x = 1–3).


$$[BH_{4-x}(CN)_x]^- + Cl_2\ (exc.) \xrightarrow{CH_2Cl_2}$$

(x = 2-3)

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Think beyond the core: New insights into the role of hydrophilic corona on the drug loading capacity of Poly(2-oxazoline)s & Poly(2-oxazine)s based micelles.

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The main aim of this work is to investigate the impact of hydrophilic corona on the drug loading capacity (LC) of polymeric micelles (PM). Generally, PM are characterized as core-shell structure[1]. Besides ultra high loading capacities[2], recently we have found that a small chemical change in the core forming block has significant impact on the drug LC of Poly(2-oxazoline)s & Poly(2-oxazine)s based amphiphilic triblock (A-B-A) (A=poly(2-n-methyl-2-oxazoline) copolymers for the highly hydrophobic drugs paclitaxel (PTX) and curcumin (CUR) respectively [3]. In order to further investigate this structure property relationship we have extended our studies to the shell forming block of the micelles. To put into action, we have synthesized six new triblock copolymers, four with poly(2-ethyl-2-oxazoline) (A*) (A*-B-A*) and two with A and A* (A*-B-A) as hydrophilic domains respectively. Upon testing the solubilizing capacity of these amphiphiles for PTX & CUR while keeping the core constant, surprisingly we found that, high LCs (as in case of A-B-A block copolymers) were not achieved in the case of A*-B-A* while A*-B-A have given somewhat higher LCs as compared to A*-B-A* but still lower than A-B-A amphiphiles. The order of LCs from A-B-A > A*-B-A > A*-B-A* clearly indicates that not only core forming block but the corona of the micelles has also the significant impact on drug loading and the build-up of micellar architecture. This study opens a new avenue for the further exploration of micellar morphology.

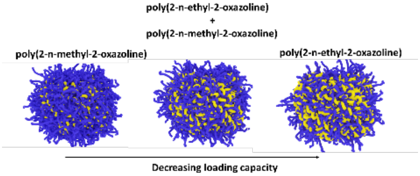

Figure 1: Impact of micellar corona on the drug loading capacity & morphology of micelles.

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Hydrogen-Bond Directed Aggregation of Diketopyrrolopyrroles into a Columnar Liquid-Crystalline Phase

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The control of self-assembly directed by H-bonds has been widely investigated for many dyes such as merocyanines[1] and perylene bisimides[2], giving access to assemblies with desired functional properties and characteristic optical signatures. Interestingly, despite the wide application of diketopyrrolopyrroles (DPP) dyes as brilliant red color pigments ("Ferrari Red") and semiconductors in organic electronics,[3] the self-assembly of DPPs in solution and in the liquid-crystalline (LC) state has been barely explored.

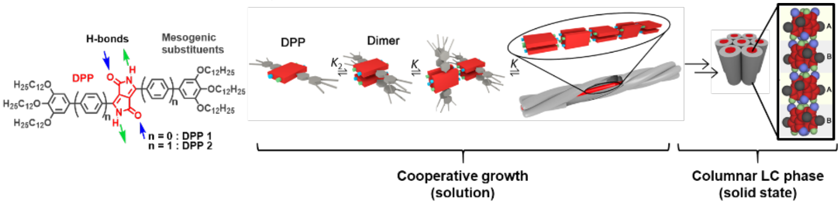

Figure 1. *Molecular structure of* ***DPP 1*** *and* ***DPP 2*** *and schematic illustration of the assembly in solution and the liquid-crystalline state.*[4,5]

In this work we present the first example for the self-assembly of DPP dyes guided by H-bonding between non-alkylated lactam units, leading to a columnar LC phase with an exotic packing of two dimers with mirror-image configuration.[4] Structural modification further allowed the preparation of highly anisotropic microfibers by self-assembly assisted electrospinning.[5]

[1] S. Yagai, Y. Nakano, S. Seki, A. Asano, T. Okubo, T. Isoshima, T. Karatsu, A. Kitamura, Y. Kikkawa, *Angew. Chem. Int. Ed.* **2010**, *49*, 9990–9994.
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Magnetic supraparticle microrods from superparamagnetic nanoparticles: a magnetically switchable material with versatile optical properties

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Figure 1. Scheme of the anisotropic optical behaviour of a superparamagnetic microrod.

The work shows the versatile application potential of super-paramagnetic microrods, a kind of anisotropic supraparticle[1] that can be obtained by assembling superparamagnetic iron oxide (mainly magnetite, Fe_3O_4) nanoparticles in a simple wet chemical synthesis process where a silane acts as an interparticular adhesive. The resulting superparamagnetic microrods have a relatively wide size distribution, a high saturation magnetization and a surface potential almost identical to that of pure iron oxide. In contrast to the nanoparticular building blocks, the superstructures exhibit an optical anisotropy that leads to different optical properties depending on the viewing angle. These differences are caused by the distinct behaviour with respect to absorption and reflection and are not shifted equally over all wavelengths, but nonlinearly. For example, by superimposing two absorption spectra, which are measured in different directions with respect to the microrod orientation, an intersection point is created in the spectral curves, whereby the exact position depends on the microrod surface.[2] Accordingly, even a simple silica modification leads to new, viewing angle-dependent optical properties. In addition, a wavelength-dependent material with switchable isotropic-anisotropic optical properties can be obtained by modifying the microrods with an organometallic framework (MOF), which absorbs in a different wavelength range and luminesces isotropically.[3] Furthermore it is possible to use the microrods on a magnetic stray field landscape, to get a magnetically controllable, diffraction grating-like optical element for electro-magnetic waves in the visible spectrum.[4]

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Rare Earth Metal Coordination Compounds with 4'-Phenyl-2,2':6',2''-Terpyridine

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Rare earth metal complexes with a 2,2':6',2"-terpyridine are known for several decades.[1] However, the interest to them has significantly increased only in the latest years. One of significant feature of terpyridines is a sensitization of lanthanide emission, especially of Eu^{III} – quantum yields are going up to 45%.[2] Substituted terpyridines and their coordination compounds are not so well studied. A large number of 4'-subsituted terpyridines is known,[3] providing a possibility for wide research.

Products of metal chlorides and 4'-phenyl-2,2':6',2"-terpyridine (ptpy) with various structures were obtained: [ScCl$_3$(ptpy)]; $^{1}_{\infty}$[MCl$_3$(ptpy)] (La – Nd); [MCl$_3$(ptpy)(py)] (Pr – Lu, Y). Compounds obtained with typical NIR emitters (Pr^{III}, Ho^{III}, Er^{III}, Tm^{III}) show an emission in the visible region. Several cases of such behavior are known for coordination compounds, but it was never observed for all those four metals within one system at once.

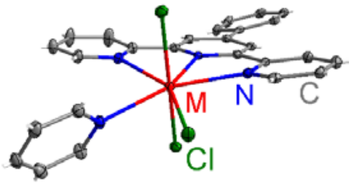

Figure 1. A X-ray crystal structure of a complex unit of [MCl$_3$(ptpy)(py)].

For Eu^{III}, further complexes with ptpy were obtained of common formula [EuX$_3$(ptpy)(L)] (X = Cl, NO$_3$; L = acetone, thf, acetamide, H$_2$O). On their example, influence of anions and co-ligand on the luminescence of Eu^{III} in ptpy complexes could be studied, for future development of coordination polymers with 4'-phenyl-2,2':6',2"-terpyridine derivatives where phenyl group is modified with various coordination groups. For chloride products, co-ligand coordinated could be fairly easy exchanged on one of several 4,4'-bipyridines, leading to the formation of isostructural dinuclear complexes with various metal connection mode.

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Coherent Three-Dimensional Fluorescence Spectroscopy of the Dianion of Tetraazapentacene

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Electronic multidimensional (MD) spectroscopy, the optical analogue of MD nuclear magnetic resonance (NMR) spectroscopy is a powerful technique to probe electronic structure of quantum systems. We recently developed a 1 kHz shot-to-shot operating single-beam setup that uses fluorescence as an observable.[1,2] With this, we are able to acquire various types of three-dimensional (3D) spectra simultaneously, background-free and within a few minutes, what is challenging to realize with conventional noncollinear methods. The key technique we use is phase cycling – a procedure that allows to isolate multiple spectra without aliasing.[3] Here we demonstrate our novel approach on the dianion of TIPS-Tetraazapentacene.[4,5] Various 3D spectra could be isolated that provide rich information up to sixth order in perturbation theory, e.g. about vibronic coupling, nuclear wavepacket dynamics, highly-excited states and more.

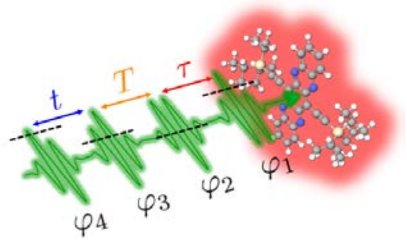

Figure 1. A sequence of four phase-coherent ultrashort pulses used for acquiring 3D spectra.

[1] S. Draeger, S. Roeding, and T. Brixner, *Opt. Express* **2017**, *25*, 3259-3267.
[2] S. Mueller et al., *J. Phys. Chem. Lett.* **2018**, *9*, 1964.
[3] H.-S. Tan, *J. Chem. Phys.* **2008**, *129*, 124501
[4] L. Ji et al., *Angew. Chem. Int. Ed.* **2016**, *55*, 10498-10501.
[5] L. Ji et al., *J. Am. Chem. Soc.* **2017**, *139*, 15968-15976.

Living Supramolecular Polymerization of Dye Aggregates with H- and J-Type Exciton Coupling

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Kinetic effects in supramolecular polymerization are essential, playing an important role in the structure and functions of the self-assembled aggregates. One strategy to control the kinetics of an aggregation process is the seeded polymerization concept, which consists of the induction of supramolecular polymerization of kinetically trapped building blocks by addition of seeds (small aggregates acting as nuclei).[1]

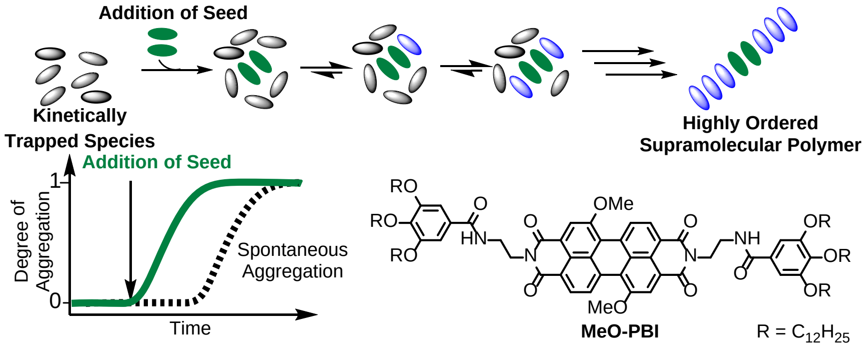

Figure 1. Illustration of the concept of seeded polymerization and molecular structure of **MeO-PBI**.

In our previous studies we have successfully applied the concept of seeded supramolecular polymerization in perylene bisimide (PBI) dye aggregates.[2] In the present work, we demonstrate that this approach can be also employed to transform kinetically trapped non-fluorescent H-aggregates of a dimethoxy-substituted PBI dye (**MeO-PBI**) into highly emissive J-aggregates by an innovative living supramolecular polymerization mechanism.[3] This is an unprecedented approach to control the kinetics of supramolecular polymerization and to obtain out-of-equilibrium polymers with low polydispersity, narrow size distribution and photofunctional properties.

[1] S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu, M. Takeuchi, *Nat. Chem.* **2014**, *6*, 188-195.
[2] S. Ogi, V. Stepanenko, K. Sugiyasu, M. Takeuchi, F. Würthner, *J. Am. Chem. Soc.* **2015**, *137*, 3300-3307.
[3] W. Wagner, M. Wehner, V. Stepanenko, S. Ogi, F. Würthner, *Angew. Chem. Int. Ed.* **2017**, *56*, 16008-16012.

Simulation of Photochemistry and Time-resolved Spectroscopy in Organic Molecules

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Roland Mitrić

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The ultra-fast photodynamics of organic molecules can be measured by femto-second laser spectroscopy. The measured signals usually contain a variety of properties of the system under investigation and are composed of intricate and elaborate patterns which require a careful and meticulous analysis. To disentangle the high complexity of the obtained data we use theoretical models to simulate the underlying processes. The cooperation of theoretical and experimental work leads to a deeper understanding of the light-induced dynamics that are observed. The ultra-fast dynamics of Benzocyclobutene-1,2-dione were simulated using field induced non-adiabatic surface hopping (FISH) molecular dynamics simulations.[1] Another example of successful cooperation of experimental and theoretical work is the elucidation of the dynamics of the photoelectron spectrum of the methyl-ally radical. [2] One main feature is the direct resolution of the dynamics in excited electronic states. The electronic character in the ground state can change drastically upon excitation. The investigation of para-Xylylene by time-resolved photoelectron spectroscopy (TRPES) combined with FISH simulations revealed the biradical nature of the excited state prevalent shortly after excitation.[3]

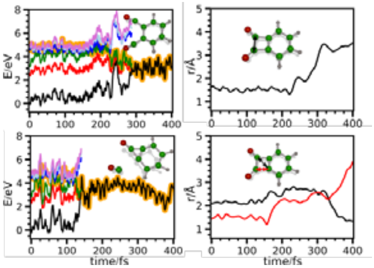

Figure 1. Energy and distances along selected trajectories of Benzocyclobutene-1,2-dione after photo excitation.[1]

[1] X. Ma, M. Wenzel, H. Schmitt, M. Flock, E. Reusch, R. Mitrić, I. Fischer, T. Brixner, *Phys. Chem. Chem. Phys.* **2018**, *20*, 15345-15444.

[2] A. Röder, K. Issler, L. Poisson, A. Humeniuk, M. Wohlgemuth, M. Comte, F. Lepetit, I. Fischer, R. Mitrić, J. Petersen *J. Chem. Phys.* **2017**, *147*, 013902.

[3] K. Issler, A. Röder, F. Hirsch, L. Poisson, I. Fischer, R. Mitrić, J. Petersen, *Faraday Discuss.* **2018**, *20*, 15345-15444

Mimicking nature to solve the problem of poor water solubility of alkaloids by means of Ionic Liquid and Natural Deep Eutectic Solvent formation

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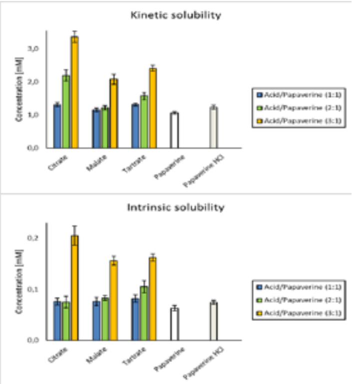
The implementation of new reliable product development programmes for Active Pharmaceutical Ingredients (API) with low cost and time range is very interesting for the pharmaceutical industry, because very few of the evaluated drugs in clinical tests actually make it to the market, decreasing the accessibility of more efficient therapies. Due to solids are easy to handle and offer a high thermal stability, up to 90% of drugs are available in their solid form. Therefore, the design and synthesis of new solid forms offer a new way of improving their efficiency by enhancing its solubility, dissolution, thermal stability, bioavailability and/or pharmacokinetics.[1]



Kinetic and intrinsic solubility of created Deep Eutectic Solvents/Ionic Liquids

Since large counterions are able to prevent strong lattice forces within the crystals, it was aimed to use those large natural compounds within a huge screening program for Ionic Liquid (IL) and Deep Eutectic Solvent (DES) formation of basic, poorly water soluble APIs, in order to enhance their solubility.[2,3]

[1] S. Domingos, M. T. Duarte, *J. Pharm. Pharmacol.* **2015**, *67*, 830-846.
[2] A. T. Serajuddin, *Adv. Drug Deliv. Rev.* **2007**, *59*, 603-616.
[3] Y. H. Choi, G.-J. Verpoorte, *Plant Physiology*. **2011**, *156*, 1701-1705.

Entwicklung eines Programms zur Berechnung, Visualisierung und Auswertung von Wellenfunktionen im eindimensionalen Kastenpotential

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Es wurde ein Programm für den Versuch „Teilchen im Kasten“ des physikalisch-chemischen Praktikums des Bachelorstudiengangs Chemie entwickelt. Ziele waren, im Vergleich mit dem zuvor verwendeten Mathematica-Skript eine einfachere Bedienung und eine höhere Ausführungsgeschwindigkeit zu erzielen, sowie neue Potentialtypen und andere Funktionen wie die zeitabhängige Simulation von Wellenpaketen zu implementieren.

Die betrachteten Potentiale $V(x)$ sind dadurch gekennzeichnet, dass sie stückweise konstant mit unendlich hohen Barrieren sind, d. h. es gibt ein $x_0 \in \mathbb{R}$ und ein $x_n \in \mathbb{R}$ mit $x_0 < x_n$, für die $V(x) = \infty$ für $x < x_0$ oder $x \geq x_n$ gilt. Weiterhin ist $V(x) = V_i$ für $x \in [x_i, x_{i+1})$ mit $i = 0; 1; \ldots n\text{-}1$.

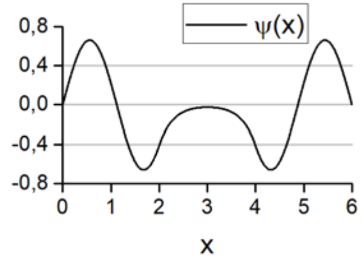

Abbildung 1. Beispiel einer berechneten Wellenfunktion im Doppelmuldenpotential

Die Berechnung der Wellenfunktionen erfolgt nicht (wie zuvor) numerisch nach dem Runge-Kutta-Verfahren, sondern analytisch. Dazu wird die Wellenfunktion analog zum Potential stückweise definiert. Die Stücke werden abhängig von der Relation zwischen Potential und Energie (gleich, kleiner oder größer) als lineare Funktion oder als Linearkombination von Exponentialfunktionen oder von Sinus und Cosinus angesetzt. Die Koeffizienten werden so gewählt, dass Kontinuitätsbedingungen an den Unstetigkeits-stellen des Potentials x_i und die Normierungsbedingung erfüllt sind.

Die Kontinuität der Wellenfunktion an der Stelle x_n muss durch geeignete Wahl der Energie erfüllt werden. Dies wird durch die Implementierung des Newton-Verfahrens automatisiert.

Zur Auswertung werden die Aufenthaltswahrscheinlichkeiten in den verschiedenen Potentialabschnitten sowie der Ortserwartungswert berechnet. Auch ist es möglich, die Wahrscheinlichkeitsdichte von beliebigen Superpositionen der Eigenfunktionen zeitabhängig zu berechnen und darzustellen.

Synthesis of Helically Chiral Organoboron Compounds

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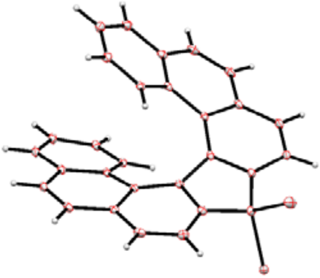

Figure 1. Single crystal structure of helical four-coordinate boron molecule

Chirality is the increasingly important concept in the design of functional organic π-conjugated materials. Our approach to synthesize chiral molecules is based on the introduction of boron atoms into biaryl or oligoaryl precursors. Subsequent formation of dative bonds between boron atoms and adjacent heteroatoms entails the formation of helices[1,2]. These helically chiral four-coordinate boron compounds are expected to show attractive (chir)optical properties such as high absorption dissymmetry factors and high fluorescence quantum yields in solution and solid state due to the presence of twisted structures[3]. The challenge is to obtain materials featuring high racemization barriers. Such inherently strong chiral properties would facilitate exploration of chirality in single-molecule devices and the design of novel chiral materials for technological applications. Here we address the synthetic aspects of helical four-coordinate boron compounds with fully π-conjugated systems.

[1] F. Jäkle, *Chem. Rev.* **2010**, 110, 3985-4022.
[2] L. Ji, S. Griesbeck, T. B. Marder, *Chem. Sci.* **2017**, 8, 846-863.
[3] V. F. Pais, M. M. Alcaide, R. Lopez-Rodriguez, D. Collado, F. Najera, E. Perez-Inestrosa, E. Alvarez, J. M. Lassaletta, R. Fernandez, A. Ros, U. Pischel, *Chem. Eur. J.* **2015**, 21, 15369-15376.

IR/UV Ion-Dip-Spectroscopy or Why We Use a Free Electron Laser

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[2] *Institute for Molecules and Materials, Radboud University*

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We employ IR/UV- Ion-Dip-Spectroscopy (IR-IDS) for the analysis of gas-phase reactions and isolated reactive molecules, like radicals, carbenes and biradicals. This double-resonance spectroscopic method delivers mass selected IR spectra, which are used for characterization of simple and complex molecular beams. Due to the low IR and UV absorption cross-section of polycyclic aromatic hydrocarbons and low concentrations in the gas phase, a high flux tunable IR source is required. Here we use an IR Free Electron Laser (FELIX, Netherlands), which can be scanned over the typical IR fingerprint region and has enough power for sufficient IR excitation. Consequently, the IR data is compared to DFT-Calculations for product identification and analyses of possible Reaction pathways.

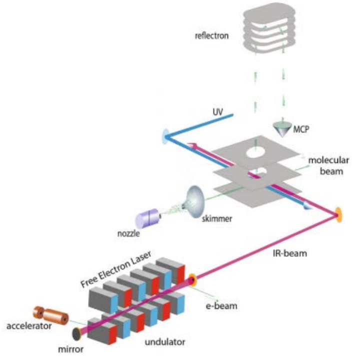

Figure 1. IR/UV-IDS Setup with the Free Electron Laser for Infrared eXperiments FELIX.[1]

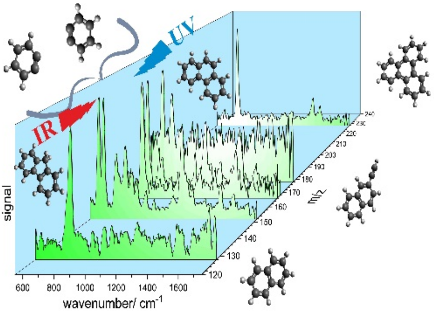

Figure 2. IR spectra of all identified masses shown as 3d-map.

[1] A. Rijs and J. Oomens, Gas-Phase IR Spectroscopy and Structure of Biological Molecules, Springer International Publishing, **2015**

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78	Panchal	Santosch	Nowak-Król
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1	Renner	Rebecca	Würthner
32	Roos	Lena	Krüger
46	Sapotta	Meike	Würthner
55	Schamburger	William	Bringmann
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73	Müller	Stefan	Brixner
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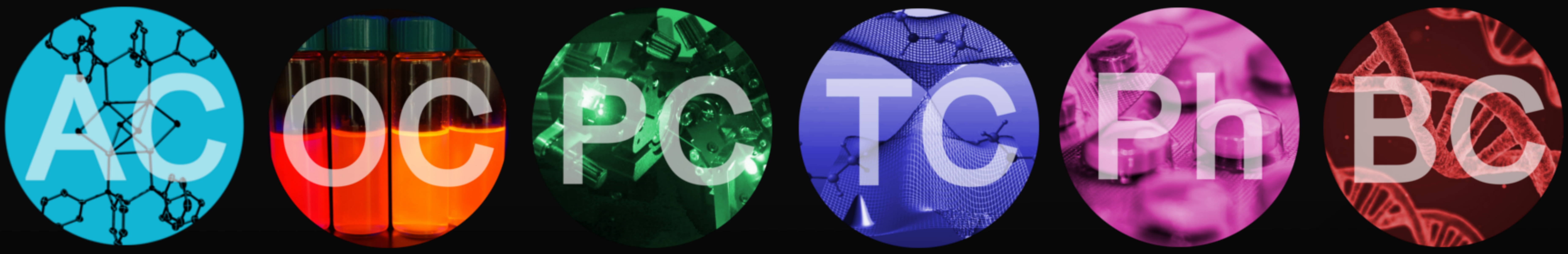

Programmablauf
ChemSyStM 2018

12:15	Begrüßung
12:30	Vortrag Herr Gerhard Karger, Vorstellung der GDCh
12:45	Vortrag Herr Christian Lange, VAA "Mein erster Arbeitsvertrag"
13:45	Posterappetizer (Kurzvorträge)
14:30	Postersession
17:00	Sektempfang
17:15	Abendvortrag

Preisverleihung im Anschluss