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The Magic of Polypnictogen-based Chemistry

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Organometallic polypnictogen compounds are an important class of compounds, valuable for many applications. Our interest is dedicated to pnictogen-rich organometallics, which usually can be synthesized from the E₄ allotropes (E = P, As). Therefore, we have developed special approaches for the activation of the E₄ molecules. Also, we created novel E₄-transfer reagents to avoid the handling hazardous starting materials. The talk will give an overview about the latest developments in the area of E₄ activation^[1] and the stage of the use of the transfer reagents in main group and transition metal chemistry.

Moreover, pentaphosphaferrocene, [Cp*Fe(η⁵-P₅)], the P-rich congener of ferrocene, can be used as a starting material in different directions: (i) in redox-processes where charged anionic and cationic polyphosphorus moieties are obtained, (ii) in the reaction with Cu(I) halides where nano-sized inorganic fullerene-like molecules are formed. Thus, the second part of the talk is dedicated to recent results in redox chemistry of pentaphosphaferrocene^[2] and in the latest giant spheres obtained.^[3]

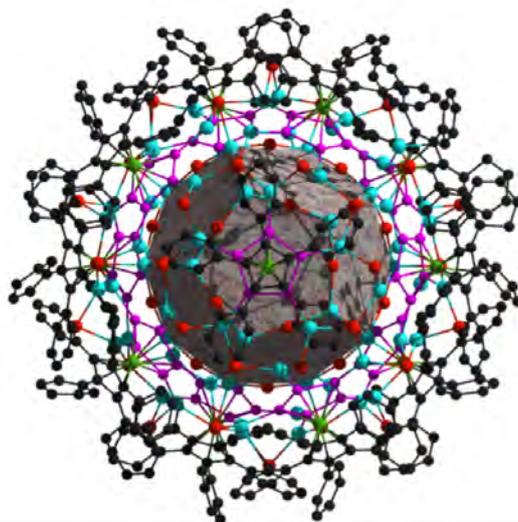


Figure 1. Molecular structure of an organometallic supersphere.

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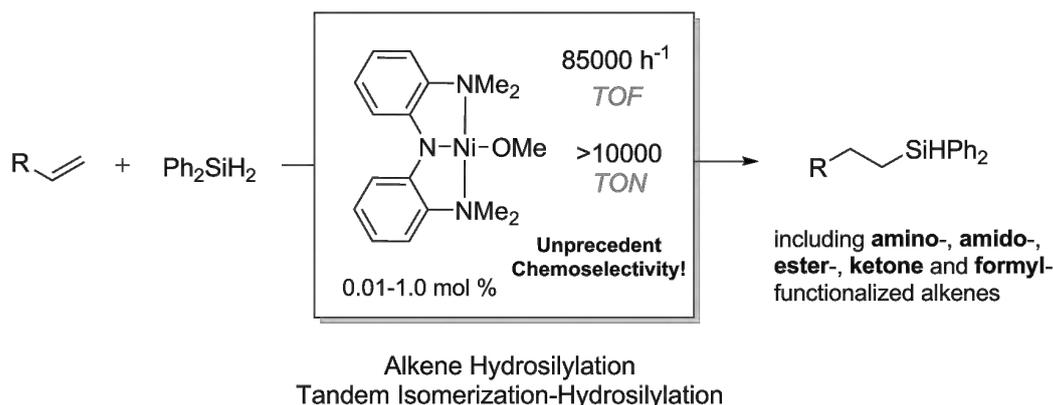
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Chemoselective Alkene Hydrosilylation Catalyzed by Nickel Pincer Complexes

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Hydrosilylation of alkenes is widely used for the production of numerous consumer goods and fine chemicals.^{1,2} Platinum catalysts, such as Speier's³ catalyst and Karstedt's⁴ complex, are still most often used for this reaction. However, the high cost and low abundance of Pt motivates the development of alternative catalysts based on more abundant and economical metals.



The bis(amino)amide nickel alkoxy complexes, [(^{Me}N₂N)Ni-OR] (R = Me, iPr, tBu), efficiently catalyse anti-Markovnikov hydrosilylation of terminal alkenes without pre-activation. An excellent functional group tolerance was demonstrated: alkenes containing halogens, ester-, amido-, sulfonylamido- and free amino-groups were hydrosilylated with good yields. Furthermore, in contrast to previously reported Ni-catalyzed hydrosilylations of C=O, keto- and formyl groups were tolerated. Also, the system showed ability to promote isomerization-hydrosilylation of functionalized internal alkenes to give terminal alkylsilanes. The starting [(^{Me}N₂N)Ni-OR] complex *in situ* produces [(^{Me}N₂N)Ni-Alkyl] which is identified as the resting state of the catalysis. The mechanistic studies, as well as development of other Ni-based catalytic systems for hydrosilylation are ongoing.

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Chiral (NH)₂P₂ Macrocyclic Iron(II) Complexes: Design and Application in the Highly Enantioselective Transfer Hydrogenation of Ketones

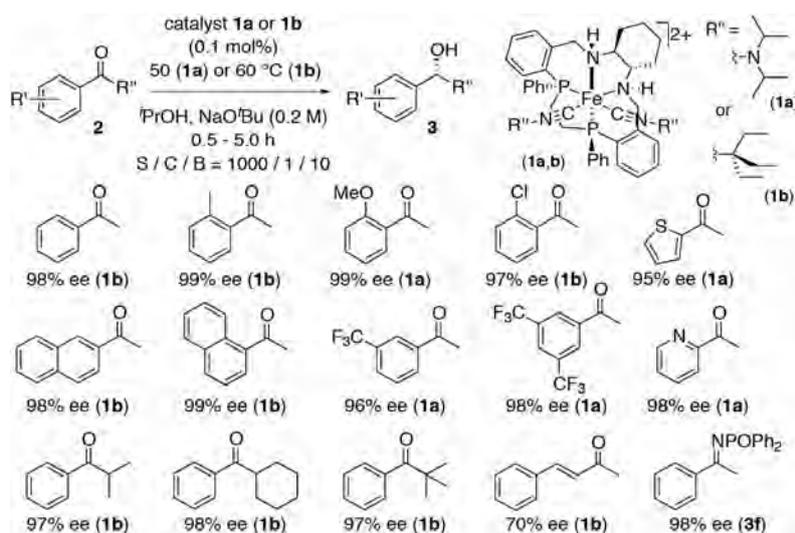
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¹ETH Zurich

In the past decade, great progress has been made to find cheap, environmentally benign 3d metal analogues as alternatives to expensive and often toxic precious metal catalysts, and iron is of central interest.^[1] However, a major problem still is the inherent lower stability of these complexes as the metal-ligand bonds are weaker if compared to their 4d and 5d analogues. To this end, we recently developed chiral tetradentate N₂P₂ macrocyclic ligands that give stable, diamagnetic iron(II) complexes.^[2,3]

We show here that the corresponding bis(isonitrile) iron(II) complexes bearing a C₂-symmetric diamino (NH)₂P₂ macrocyclic ligand efficiently catalyze the asymmetric transfer hydrogenation of polar bonds of a broad scope of substrates (ketones, enones, and imines) in high yield (up to >99.5%) and with excellent enantioselectivity (up to 99% ee).^[4] The substrate scope includes challenging ketones like arylalkyl ketones containing bulky alkyl groups, *ortho*-substituted acetophenones, acetophenones, acetonaphthones, and acyl-substituted heterocycles, i.e. acyl pyridines and acyl thiophenes. Turnover frequencies of up to 1950 h⁻¹ were achieved while keeping the catalyst loading low (generally 0.1 mol%). The ancillary isonitrile ligand (*C*-isonitriles and *N*-isonitriles were used) have a large and unprecedented influence on the activity and selectivity of the catalyst, which is exploited for the fine-tuning of the catalyst to achieve optimal results for specific substrates. Furthermore, preliminary tests support a homogeneous mechanism.

In sum, this is the first chiral iron(II) catalyst for the transfer hydrogenation of ketones that combines high activity and excellent enantioselectivity for a wide scope of substrates.



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Two Synthetic Approaches for one target: Single Molecule Magnet Behaviour

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The first observation of a magnetic bistability phenomenon from a purely molecular origin has been reported by Sessoli *al.*¹ in 1991, on Mn₁₂ acetate complex. Since this pioneering result, molecules exhibiting a slow relaxation of their magnetization are named single molecule magnets or SMMs and have been widely studied. Single molecule magnet behaviour is generally associated and represented by two characteristics: **(1)** a large magnetic anisotropy characterized by a large negative value (*D*) and **(2)** a large ground state spin (*S*). Up to now, peculiar attentions have been devoted to the synthesis of 3d and heterometallic 3d-3d' complexes.² But recently, in the search for more efficient SMMs, it has been demonstrated that the incorporation of a highly anisotropic 4f ions into 3d matrices can enhance the SMM properties.³ Furthermore, Powell *al.*⁴ in 2008, revealed that the combination of a highly anisotropic 4f ion with a highly isotropic 3d ion such as Cr^{III} ion can led to the formation of 3d-4f clusters with higher blocking temperature.

In the quest of new efficient SMMs, two synthetic approaches are currently under exploration in our group: **(1)** synthesis of heterometallic Cr-Ln molecular materials and **(2)** polyoxometalate materials. As metal-oxo cluster materials containing transition metal ions in their higher oxidation state (mainly Mo and W), polyoxometalates or POMs are a virtually inexhaustible reserve of robust and structurally diverse compounds for future applications in catalysis⁵ and electronic devices.⁶

We will present herein new developments and promising results in molecular magnetism based on the two approaches cited above. In a first instance, we will show a new family of isostructural mononuclear 4f polyoxometalates. All compounds have been fully characterized by single crystal X-ray diffraction techniques, ATR-FTIR spectroscopy and photoluminescent properties were also investigated. The full magnetic behaviour (dc and ac magnetic susceptibility measurements) of each compound was studied in detail. We also report here a new family of heterometallic Cr^{III}-Ln^{III} complexes. Crystal structure determinations revealed that the dysprosium and the terbium derivatives crystallize both into two polymorph forms (crystal systems: triclinic and monoclinic). Full magnetic behaviour investigations showed that the Dy^{III} and Tb^{III} complexes exhibit single molecule magnet behaviour.

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Self-assembly of 3d-5f Molecular Magnets from Pentavalent Uranyl

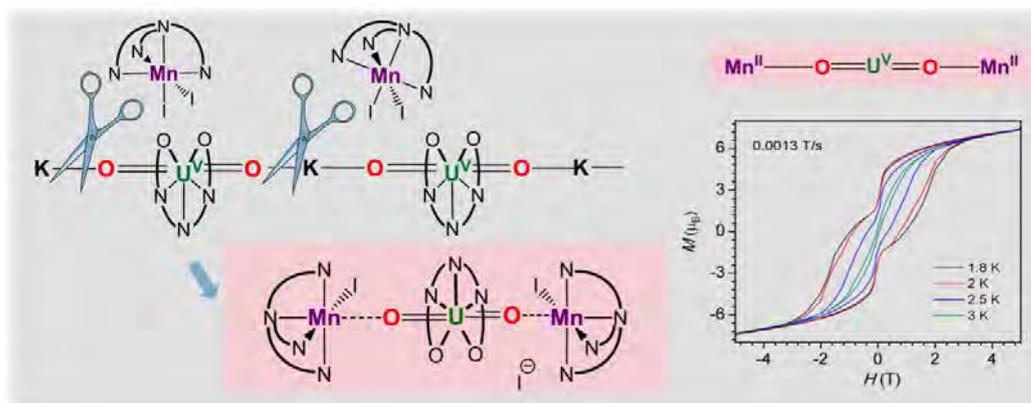
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The design of multinuclear molecular actinide complexes is of high current interest for the development of actinide based single molecule magnets. A key property of an uranyl(V) moiety is its ability to bind another metallic center through the axial oxygen (commonly known as cation-cation interaction, CCI) leading to homometallic or heterometallic assemblies. We have recently shown that a suitable choice of ligand and conditions can lead to the isolation of assemblies with various topologies and nuclearities.^{1,2}

Such assemblies show unambiguously an intermetallic communication that can be tuned by appropriate structural modifications to design complexes behaving like single molecule magnets (SMM). SMM are attractive molecules with a slow relaxation of the magnetization from a purely molecular origin. To improve the properties of SMM, a high spin ground state and a high magnetic anisotropy are required. In spite of the high single ion anisotropy of uranium, only few uranium based SMMs have been reported to date. We have recently shown that an SMM with enhanced properties can be obtained from the association of the high spin Mn²⁺ ion and of the highly anisotropic uranyl(V) in a large wheel shaped Mn₆U₁₂ cluster.³

Here we will report that the topology of 3d-5f assemblies built from pentavalent uranyl can be tuned by the stoichiometry and the control of the coordination sphere of the d-block metal. This novel rational synthetic approach leads to the formation of a polymeric structure⁴ with single chain magnet properties and to the assembly of discrete trinuclear heterometallic 3d-5f uranyl(V) based complexes. In particular, a TPA-capped Mn(II) complex allows the controlled formation of a U Mn₂ trinuclear complex⁵ that exhibits SMM behaviour with the highest relaxation barrier reported to date for a mono-uranium system (barrier of 81 ± 0.5 K arising from intramolecular Mn-U exchange interaction) and a open magnetic hysteresis loop at T < 3 K.



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On the Synthesis, Biological Evaluation and Use of Metallocenyl DerivativesJ. Hess¹, M. Patra¹, A. Leonidova¹, V. Pierroz¹, S. Ferrari¹, G. Gasser^{1*}¹University of Zurich

In the last years, metallocene-containing compounds have been intensively explored as promising anticancer or antimalarial drug candidates.^[1] An improvement in the pharmacokinetic properties of the original drug was achieved through the conjugation of metallocenyl moieties to the initial drug. This is exemplified by ferroquine, which is a ferrocene derivative of the antimalarial drug chloroquine, which was found to be active on chloroquine-resistant strains. Thus, there is doubtlessly a high demand on novel synthetic strategies to prepare new functionalized metallocenyl derivatives. With this in mind, our group has recently reported the synthesis of diverse biologically relevant metallocenyl derivatives. These synthetic pathways give access to new organometallic conjugated moieties, which are valuable chemical entities in a broad biological context.^{[2], [3], [4]}

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Vibrational spectroscopy on functionalized and chiral monolayer protected gold clusters

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The structure of monolayer protected gold clusters can be described by the divide-and-protect-model,^[1] i.e. they are built up from a gold core and a protecting shell of gold-thiolate units.

Vibrational spectroscopy is one way to discriminate bond strengths and geometry sensitively.^[2,3] The low-wavenumber region, which contains the Au-S and Au-S-C vibrations, can be investigated with far-infrared and Raman spectroscopy. With these means we studied thiolate-protected gold clusters with surface structures composed of monomeric (S-Au-S) and dimeric (S-Au-S-Au-S) binding units.

DFT calculations on the well-known Au₃₈L₂₄ cluster allow discriminating the spectral contributions of such units. The assignment can be transferred to clusters with different surface composition. A systematic shift of the Au-S-C bending allows estimating the number of monomeric and dimeric units. Further, vibrational spectra of bimetallic Au-Ag clusters were studied and Au-S and Ag-S vibrations were discriminated. The catalytic activity of bimetallic clusters depends on the availability of the active metal (core vs. staples) to the substrate and vibrational spectroscopy is therefore a valuable tool for their characterization. Moreover, the ligand type used for the stabilization of the cluster influences the low-wavenumber range of the vibrational spectrum. Raman measurements reveal information about ligand-ligand interactions between long aliphatic chains. The distortion of the shell upon partial ligand exchange with di-thiolate ligands is reflected in the spectra.

It was found that intrinsic chirality is a common feature of monolayer protected gold clusters. The enantiomers of Au₃₈L₂₄ could recently be separated by high performance liquid chromatography.^[4] Vibrational circular dichroism measurements on the enantiomers show that the chiral cluster transfers its handedness to the achiral ligand.^[5] Chirality transfer of surfaces to adsorbed molecules is a phenomenon playing an important role in asymmetric catalysis.

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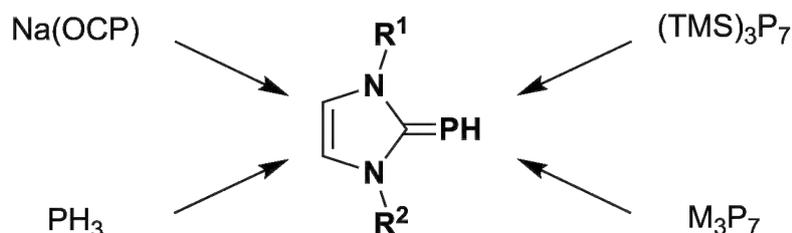
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Carbene insertion into a P-H bond: Parent phosphinidene-carbene adducts from PH₃M. Bispinghoff¹, H. Grützmacher^{1*}¹ETH Zurich

Phosphinidenes, the phosphorus analogues of carbenes, are highly reactive species and eluded isolation so far. In 1997, Arduengo and co-workers showed that substituted phosphinidenes can be stabilized by adduct formation with N-heterocyclic carbenes (NHC).[1] We have recently prepared the parent NHC=PH adduct from imidazolium chlorides and the easily accessible P⁻ transfer agents (TMS)₃P⁻ or Na(OCP) and applied this building block in the formation of carbene-supported P₃-cations and radicals.[2]

Herein, we report the synthesis of numerous parent phosphinidene-carbene adducts from halogen-free phosphorus transfer agents. Furthermore, we describe the insertion of a carbene into a P-H bond, giving access to NHC=PH adducts from PH₃ gas (Scheme 1)[3]. Finally, the influence of the steric and electronic properties of the NHC on the properties, reactivity and coordination behavior of the adducts will be discussed and their use as synthetic reagents demonstrated.



Scheme 1: Synthesis of parent phosphinidene-carbene adducts from different phosphorus transfer agents and PH₃ gas. R = Me, Et, *i*Pr, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl.

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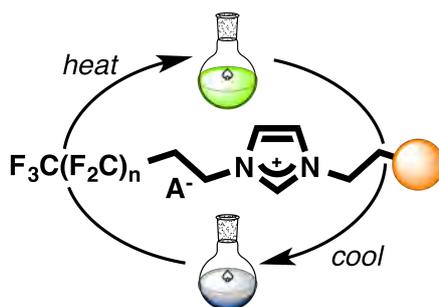
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Design and Synthesis of Perfluorinated Ionic Liquids

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Perfluorinated solvents display many desirable properties, of which *thermomorphism* is especially interesting for catalytic applications.¹ Although this approach can be generalized for catalysts and, to some extent, used in medicinal chemistry,² examples with perfluorinated ionic liquids are scarce.



We are currently investigating a series of task-specific ionic liquids bearing perfluorinated side chains along with other functional groups, which display UCST with organic solvents at higher temperatures.

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Going to Extremes: From Fluorine-Free Blue to Stable Red Emitting Iridium Complexes for LEECs

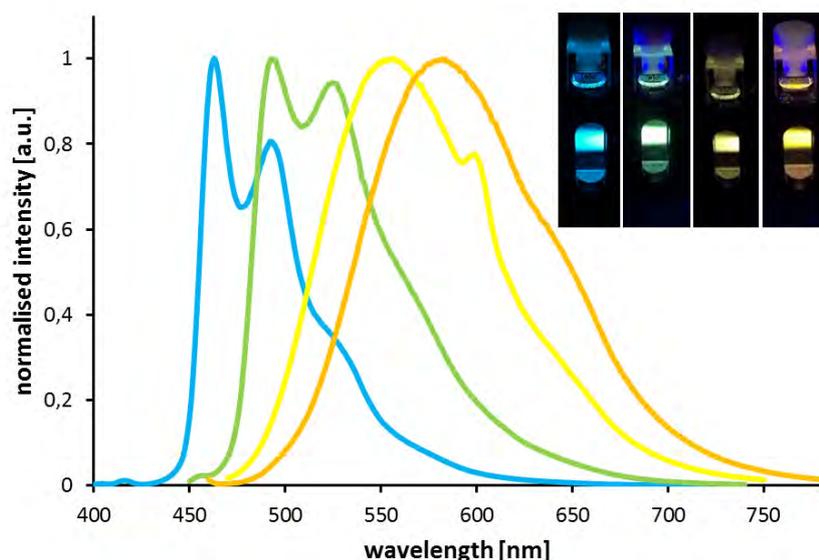
C. D. Ertl¹, A. Pertegás², H. J. Bolink², E. Ortí², E. C. Constable^{1*}, C. E. Housecroft^{1*}

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Cationic iridium(III) complexes of the type $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$ are the most intensely studied emissive compounds for light emitting electrochemical cells (LEECs). In addition to their good photophysical and chemical properties and ionic nature, emission colour tuning is straightforward due to spatial separation of the frontier orbitals, making these complexes well suited for LEEC applications.

Nonetheless, there is still a lack of stable blue and red emitters. We have introduced a series of thioether and sulfone groups on the cyclometallating ligands to investigate the influence on the emission colour.[1] Electron-withdrawing sulfone groups yielded a large blue-shift in the emission maximum and were combined with electron-rich pyrazolylpyridine ancillary ligands[2] to further blue-shift the emission without the need of fluorine groups, which have been reported to have a detrimental effect on device stability both in OLEDs[3] and LEECs.[4]

Emission red-shifts on the other hand were achieved by the introduction of benzothiazolylpyridine ancillary ligands, leading to extremely stable LEECs with the longest reported lifetimes for red-emitting iridium complexes.



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Application of ferrocene derivatives for stimuli-responsive polymers and for biosensor

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Since long time ferrocene and its derivatives have attracted the attention of the scientific and technical community because of its fascinating chemistry. Due to its easy functionalization and unusual and attractive properties, ferrocene derivatives have found different applications in material science, such as sensors, catalysts, polymers, electroactive materials and medicinal chemistry^{1,2}.

We propose two different research subjects: ferrocene-containing polymers as stimuli-responsive material and ferrocene-based trigger as biosensor.

The aim is to synthesize stimuli-responsive polymers with several ferrocene units in a linear polyurethane chain or in a linear poly(methyl methacrylate) chain and to analyze their physico-chemical changes subjecting the polymer to mechanical stress (sonication or stretching) or using techniques such as the Atomic Force Microscope.

Ferrocene derivatives can also be exploited for biomedical applications: the formation of resistant biofilms causes infection problems in the internal fixation devices³; the aim of this project is to synthesize an unsymmetrical ferrocene that could be a precursor of a new type of sensor for biomolecules, accounting for the presence of bacteria. Exploiting the rotational freedom of ferrocene, temporally restricted by intramolecular-DNA near-match pairing and then quickly released by hybridization with a fully-matching DNA strand, it is possible to identify the presence of bacteria.

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