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Ultrafast electroabsorption spectroscopy study of carrier dynamics within hybrid lead halide perovskites

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Since their first advent, hybrid lead-halide perovskite solar cells (PSCs) have kept their promises and proven to be a valid alternative to current solar cell technologies, with power conversion efficiencies rising above 20%. At this point, however, further improvements require a more fundamental understanding of some key features inherent to PSCs, such as their interfacial properties. Indeed, on top of travelling smoothly across the perovskite layer, the photocarriers must be injected efficiently into their respective extracting layers, for optimized devices.

Herein, we aim at unravelling the origin of performance inhomogeneity in PSCs by probing three essential properties : (i) the transmission of carriers across various heterojunctions, namely perovskite-*spiro*-MeOTAD and perovskite-SnO_2, (ii) the carrier recombination in the bulk material, and (iii) the carrier transport across the perovskite layer. In this respect, time-resolved electroabsorption spectroscopy (TREAS) appears as a method of choice. This technique relies on the ultrafast monitoring of the electroabsorption signal and allows to probe field-induced phenomena such as the dynamics of field screening and charge accumulation at interfaces. As a consequence, the three abovementioned properties can be successfully accessed when using this technique in combination with transient absorption spectroscopy (TAS).

In this study, two different perovskite materials ($MAPbI_3$ and $(MA, FA)PbI_{3-x}Br_x$) within four PSCs architecture exhibiting different interfacial structures have been studied by TREAS and TA spectroscopy techniques. We report a significantly more efficient electron injection at the $SnO_2/(MA, FA)PbI_{3-x}Br_x$ interface, together with a decreased bulk recombination for the latter material, compared with the standard $MAPbI_3$. This accounts for the reported higer V_{OC} and alltogether better performance of $(MA, FA)PbI_{3-x}Br_x$-based PSCs. At the material level, we assign this to the presence of nano-domains of various compositions favouring charge separation.

Unraveling the electronic states of the copper dimer using nonlinear optical spectroscopy

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High-resolution optical spectra of transition metal containing molecules and clusters are characterized by dense-lying rotational lines, originating from many overlapping vibrational and electronic bands. The copper dimer is considered to be one of the simplest transition metal systems. However, despite its hydrogen-like ground state, the electronic excited states give rise to complex spectra that are difficult to assign. As a consequence, even for the better characterized high-lying states, fundamental spectroscopic properties like molecular constants and electronic term symbols are missing.

We use Two-Color Resonant Four-Wave Mixing (TC-RFWM) methods to assign the lines of such complex absorption bands. TC-RFWM produces a spatially separated, background-free signal beam from the non-linear interaction of three input beams that overlap within the common focal point in the probe region. In the optically thin environment of a molecular beam, observable TC-RFWM signal generation requires resonance-enhancement by two transitions that share a common level. Therefore, selection rules for optical-optical double resonances apply and reduce the complex spectra to just a few rotational lines which are often assigned in a straightforward manner.

The laser ablation-based cluster source used to prepare the copper dimers in gas phase and the optical setup is described in [1]. Figure 1 shows a selected set of spectra containing rotationally resolved transitions obtained by TC-RFWM. For one isotopologue, extra lines where found and assigned to a perturbing state that is crossing the potential curve of the J-state. Some of these extra lines have already been seen before, but could not be assigned at that time. In the ongoing work, by measuring and assigning unambiguously over 600 lines in the energy range of the I-X and the J-X transitions, a rich network of perturbing states could be identified for several vibronic levels and their molecular constants could be determined. The investigations reveal a detailed picture of the complex bonding structure of this transition metal dimer. This can be used as a benchmark for prospective quantum chemical *ab initio* methods, but is also basis for future studies of heteronuclear transition metal systems.

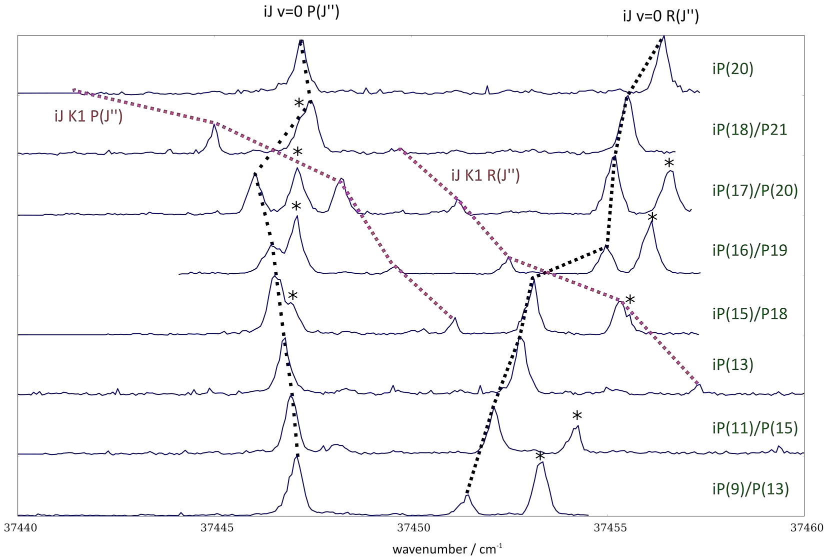

Figure 1: TC-RFWM spectra of $^{63}Cu^{65}Cu$ J-X (0-0). Single rotational lines where made visible by intermediate state labeling, pumping individual lines in the B-X (1-0) band (green labels). "i" indicates transitions in the $^{63}Cu^{65}Cu$ isotopologue, while the plain labels indicate overlapping transitions in the $^{63}Cu_2$ isotopologue. Spectral features contributed by the latter are marked with an asterisk. Within the rotational series that is pumped in $^{63}Cu^{65}Cu$, a not yet fully assigned perturbing state "K1" mixes with J, causing line shifts but also gains intensity itself.

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Protein-nucleotide interactions studied by magnetic resonance

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In this contribution we present strategies to characterize protein-nucleotide interactions in large biological assemblies using the example of the (double-) hexameric DnaB helicase from *Helicobacter pylori* with a molecular weight of 672 kDa. The binding of nucleotides (ATP-analogues and single-stranded DNA, ssDNA) to the helicase is monitored by ^{31}P,^{1}H cross-polarization experiments. The observed ^{31}P chemical-shift values allow a clear discrimination between the different nucleotides used in this work and reveal that two nucleotides of bound ssDNA can be structurally distinguished. ^{15}N,^{13}C correlation experiments highlight the role of arginine sidechains in binding to single-stranded DNA.

We further present dipolar-coupling based polarization transfer experiments from ^{31}P spins of bound nucleotides to ^{13}C or ^{15}N spins of the protein (or vice versa) to describe nucleotide binding on a molecular level (see Figure 1). Residues involved in protein-nucleotide interactions are identified in CHHP and NHHP correlation experiments.

While conventional NMR experiments on such large protein assemblies typically suffer from low signal-to-noise ratios and thus long experimental measurements times, we used Dynamic Nuclear Polarization (DNP) enhanced MAS experiments to increase the sensitivity. The samples for DNP were prepared in the absence of glycerol which results in the highest sensitivity for DnaB. The obtained spectra allow to identify spin systems of the helicase in the neighborhood of ^{31}P spins of the nucleotides. The extensive line-broadening at cryogenic temperatures is not a severe issue in this case due to the sparsity of the obtained spectra.

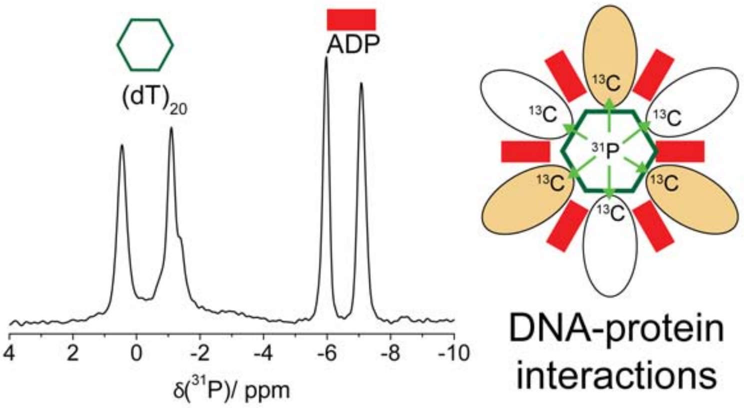

Figure 1: ^{31}P spins of bound nucleotides can be used in solid-state NMR experiments to identify helicase-nucleotide interactions.

Electrolytes induce long-range orientational order and free energy changes in the H-bond network of bulk water

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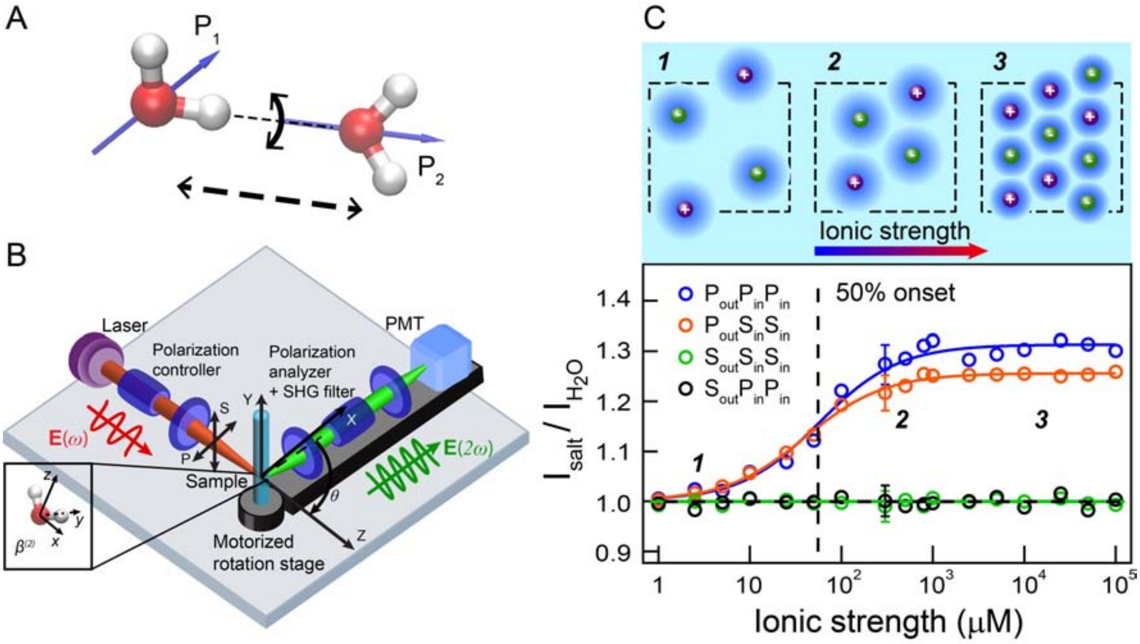
Electrolytes interact with water in many ways: changing dipole orientation, inducing charge transfer, and distorting the hydrogen-bond network in the bulk and at interfaces. Numerous experiments and computations have detected short-range perturbations that extend up to three hydration shells around individual ions. We report a multiscale investigation of the bulk and surface of aqueous electrolyte solutions that extends from the atomic scale (using atomistic modeling) to nanoscopic length scales (using bulk and interfacial femtosecond second harmonic measurements) to the macroscopic scale (using surface tension experiments). Electrolytes induce orientational order at concentrations starting at 10 μM that causes nonspecific changes in the surface tension of dilute electrolyte solutions. Aside from ion-dipole interactions, collective hydrogen-bond interactions are crucial and explain the observed difference of a factor of 6 between light water and heavy water.



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High resolution analysis and quantum dynamics of fluoroform $^{12,13}CHF_3$

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The spectroscopy of $^{12}CHF_3$ has been the basis for the study of time independent and time dependent quantum dynamics for a long time [1-9]. There have also been substantial efforts concerning the *ab initio* potential hypersurface ([10, 11] and references cited therein). We present a survey of our recent analyses ranging from the Terahertz (Far infrared) spectral range to about 3000 cm^{-1}, with particular emphasis on the pure rotational (FIR) spectra measured at the infrared beamline of the Swiss synchrotron Light Source (SLS), ν_3 fundamental (700 cm^{-1} range), the ν_2, ν_5, $\nu_3+\nu_6$ polyad (1200 cm^{-1} range), the $\nu_4/2\nu_3$ dyad (1400 cm^{-1}), the $2\nu_4$ (A_1 and E) dyad and results on the $^{13}CHF_3$ isotopomer including the ν_1 fundamental. The implications for the study of intramolecular vibrational energy redistribution (IVR) will be outlined with particular emphasis on ^{13}C isotope effects.

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Spectroscopic behavior of a water-soluble conjugated polyelectrolyte in biological environment

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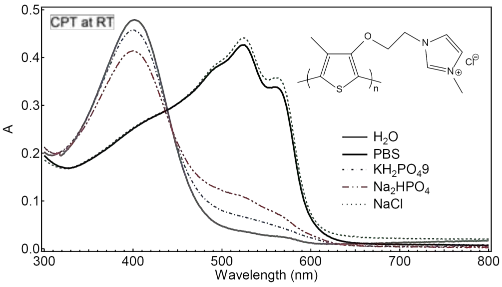
Here we present a spectroscopic study of a conjugated polyelectrolyte, which consists in a polythiophene derivative with cationic side chains that has been used as a biological sensor[1]. This work is an effort to understand the changes of photophysical properties of polyelectrolytes, depending on their conformation, which is usually linked also to the biosensing mechanism. In pure water, the polymer adopts a random-coil conformation at room temperature. On the other hand, when dissolved in an aqueous biological environment (phosphate buffered saline, PBS), the polymer chains are ordering due to the favorable interactions with the buffer ions. These different degrees of ordering in the polymer lead to color changes of the solution, with an important red-shift in the absorption spectrum in PBS. Additionally, the ratio of ordered to random-coiled polymer chains in PBS can be varied by tuning the temperature. Using resonance Raman spectroscopy combined with density functional calculations, it was shown that the ordering is linked to planarization of the polymer backbone. The excited-state behavior of the polymer in different conformations was investigated with femtosecond transient absorption spectroscopy. In the random-coil conformations, triplet state formation occurs, while in the ordered chains, a small fraction of polarons is formed, probably favored by interchain interactions.



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Direct Local Solvent Probing by Transient Infrared Reveals the Mechanism of H-Bond Induced Nonradiative Deactivation

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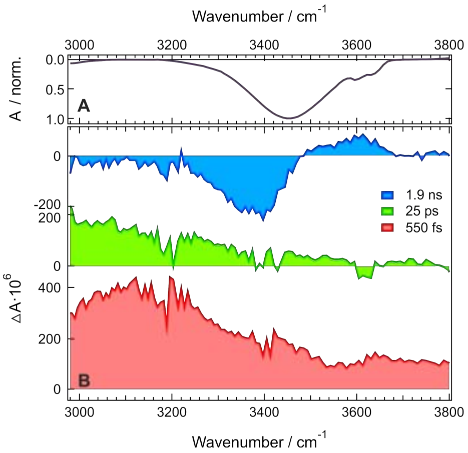
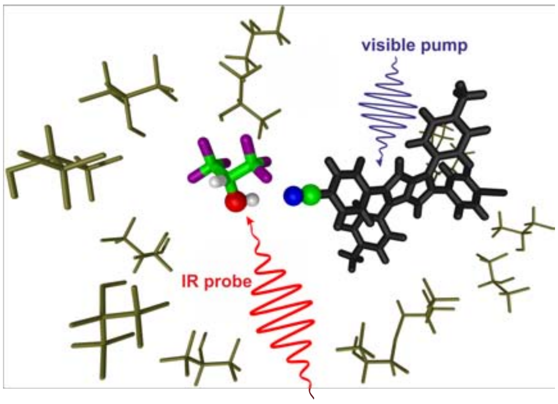
Many organic molecules undergo a substantial quenching of their charge-transfer electronic excited state in protic solvents without occurrence of excited-state proton transfer or proton-coupled electron transfer reactions. The mechanism of this H-Bond Induced Nonradiative Deactivation (HBIND) phenomenon has been elusive for a long time. By using ultrafast transient infrared spectroscopy, we show that it can be unambiguously elucidated by probing the local vibrational modes of solvent molecules coupled to the chromophore. Using such 'solute-pump/solvent-probe' approach reveals all relevant molecular steps, such as high initial coupling to the H-bonded solvent molecules, symmetry breaking, H-bond strengthening, and excitation energy dissipation to the solvent molecules. Our data reveal the key role of both solute-solvent H-bond strength and solvent-solvent intermolecular coupling for the efficient HBIND. Polarization-resolved experiments give an additional insight into the structure of a reactive intermediate.





Reaction monitoring using multiple NMR receivers

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Conventional NMR spectrometer require three main components: the superconducting magnet generating the strong magnetic field, the sensor (or probe) acting as send and receive antenna and the spectrometer console hosting the electronics required to perform the NMR experiment. The recently introduced AVANCE NEO console electronics is based on a fully modular and highly integrated RF transmit and receive (so-called transceiver) concept. Hence, each NMR channel consists of a fully autonomous and independent pulse sequence programmer, transmitter and receiver. This opens up new possibilities acquiring multi-receiver NMR experiments[1] since every AVANCE NEO console is inherently multi-receive capable with any available nucleus and probe combination. With the general availability of multi-receive capable NMR spectrometers attractive new combinations of experiments[2] will experience a fast increase in development. Multi-receive experiments are thus expected to substantially contribute in increasing the throughput of NMR spectrometer and hence pushing back one of its strongest limitations, the comparative low sensitivity.

The impact of acquiring several NMR experiments in a single shot is illustrated with an example in the field of reaction monitoring. The protodeboronation reaction of fluorinated aryl boronic acids under basic conditions allows monitoring three suitable isotopes for NMR in the course of the reaction: ^{1}H, ^{19}F and ^{11}B. Simultaneous acquisition schemes with multiple-receivers then allow obtaining kinetic data with a higher temporal resolution as compared to using a conventional acquisition with sequential data collection.

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Metal centres in EPR Spectroscopy

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Unpaired electrons are the basis of Electron Paramagnetic Resonance (EPR) spectroscopy. Electron pairing is usually energetically favorable and thus only a small fraction of systems contain native paramagnetic centres or can be put into paramagnetic states to exhibit an intrinsic EPR signal. On the other hand, it allows to use EPR spectroscopy in combination with so called site-directed spin labeling (SDSL) under a wide range of conditions.[1]

In this contribution we want to give a brief overview of the use of metal ions in EPR spectroscopy in biological systems and then focus on two examples using Mn^{2+} or Gd^{3+} as spin probes. In the first case we demonstrate, what insights can be obtained from EPR by the substitution of diamagnetic Mg^{2+} to paramagnetic Mn^{2+} in a DnaB helicase.[2] In the second example we want to demonstrate advantages and disadvantages of using high spin Gd^{3+} ions for distance measurements.[3,4]

This work is supported by SNF Grant 200020_169057.

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High Resolution ^{1}H NMR in Organic Solids at Natural Abundance

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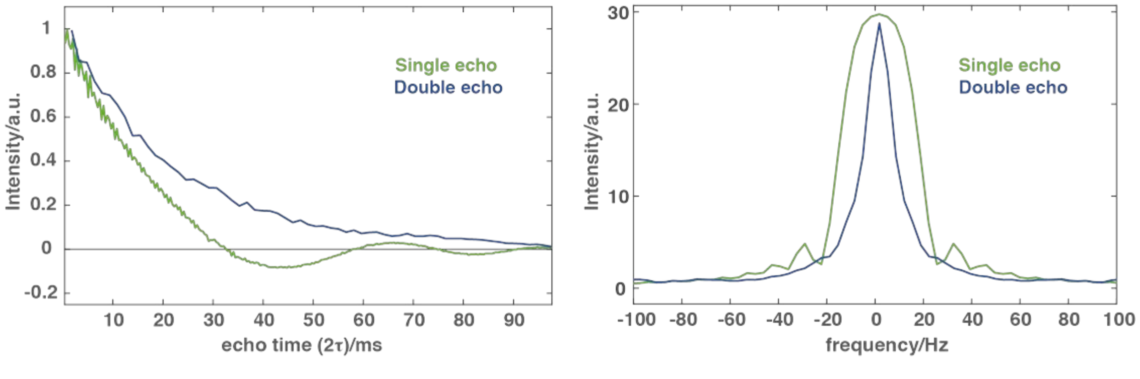
High resolution ^{1}H NMR spectra have transformed molecular chemistry over the last 60 years. However, due to the absence of molecular tumbling, in solid samples proton spectra usually have linewidths of more than 50 ppm, obscuring all chemical information. To obtain high resolution ^{1}H spectra in solids would provide a key tool for the atomic-level characterization of modern materials, especially since NMR does not require long range order.

^{1}H line broadening is primarily due to strong ^{1}H homonuclear dipolar couplings. It is possible to improve the resolution with the application of techniques such as magic angle spinning (MAS)[1] and multi-pulse sequences specifically designed to lead to homonuclear dipolar decoupling. The best results achievable today are obtained using these two techniques simultaneously, in the so-called combined rotation and multi-pulse spectroscopy (CRAMPS) approaches,[2] but linewidths are still on the order of 150 Hz.[3,4] The underlying reasons for this apparent limit on ^{1}H resolution are not understood.

Here we discover one of the limiting factors of resolution: an undecoupled residual anisotropic interaction that leads to a residual splitting. The mechanisms of line broadening were evaluated by measuring transverse dephasing times T'_2, which are indicators of the presence of non-refocusable interactions[5,6]. We have discovered an unexpected oscillating component, present in the spin-echo dephasing curves for BR-24, eDUMBO-1_{22}, LG4 and even WAHUHA. The Fourier transforms of these curves show that the oscillations correspond to an anisotropic splitting of up to 80 Hz. We also show that this residual interaction, which is one of the limiting factors on the lifetime of the decay, can be removed by the application of a double echo. As a result, the dephasing curves have slower decay, characterized by T'_2 of up to 22 ms, which corresponds to a refocused linewidth of 14 Hz.



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Detecting structure and conformation of single DNA and RNA molecules by Escape-Time Electrometry

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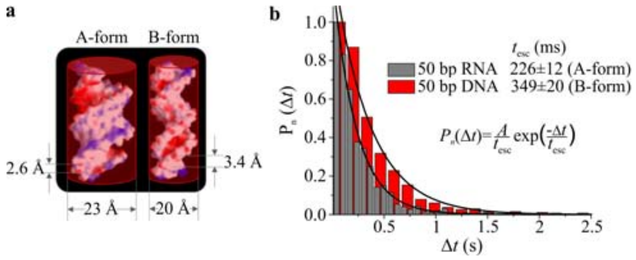
Fundamental functions of biological macromolecules, such as proteins and nucleic acids, in all living organisms strongly depend on the molecules' 3D structures, which are of great scientific interest. However, currently existing methods are bulk measurements, and further require high concentrations. We recently reported a measurement principle – escape-time electrometry (ETe) [1] – that offers a new approach to measuring the effective electrical charge, q_{m} of a single molecule in solution, in real time. Since the effective charge of a molecule in solution is a strong function of its 3D conformation [2], we have demonstrated the ability to directly link a high precision measurement of electrical charge with the 3D conformation of a charged molecule. The ETe approach exploits the spatial confinement of single molecules in an electrostatic fluidic trap. The trap is based on the spatial modulation of the electrostatic interaction energy created in a topographically-tailored fluidic nanoslit [3]. Measurement of the average escape time of single molecules from a trap of known depth allows us to determine the effective electrical charge of a molecular species with high precision.

We have performed ETe on double-stranded (ds) nucleic acids with identical base sequences, but different helical structures: A-form (dsRNA) and B-form (dsDNA). Modelling these molecules as uniformly-charged cylinders of different dimensions we also determine theoretically expected values for the effective charge, q_{c} (Fig. a, c). Our measured values of effective charge are in good agreement with the theoretical predictions, and uniquely permit the detection of important structural features of nucleic acids at the level of the single molecule (Fig. b, c).



c

50 bp	q_m (-e)	q_c (-e)
A-form (RNA)	37.7±0.7	34.4±1.7
B-form (DNA)	41.2±0.5	40.2±2.0

Furthermore, we are currently performing measurements on single-stranded (ss) RNA and DNA molecules of effectively identical sequence. In contrast to ssDNA, ssRNA is well known to form stable and varied secondary structures, which are in fact critical to biological function. While our preliminary measurements yield a single escape timescale for ssDNA, interestingly they reveal a spectrum of timescales for the equivalent ssRNA species, indicating a variety of folded states. Our results illustrate that ETe will likely enjoy broad relevance in 3D conformation determination in biology.

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Fluorophore guided RNA modeling

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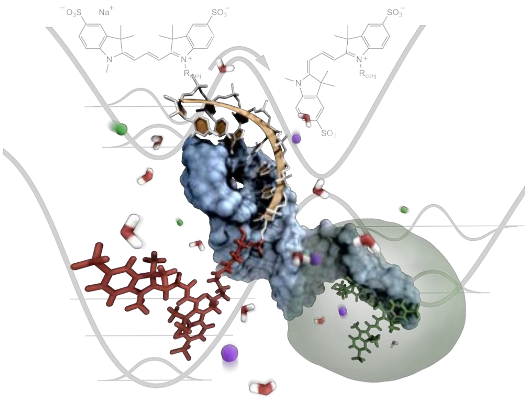
Non-coding RNAs engage in numerous cellular processes at various stages of gene expression. As a spectroscopic ruler [1] single-molecule FRET is a versatile tool to investigate the folding of RNA [2]. Yet, interconversion of transfer efficiencies and absolute distances between a donor and an acceptor fluorophore requires thorough control over both the dyes' photophysics as well as their orientation within the macromolecule [3]. We make use of the photoisomerization propensity of carbocyanines [4] to sense perturbations in their local environment. Changes to the torsional flexibility of the polymethine scaffold are probed by time-resolved fluorescence anisotropy and RNA-induced fluorescence enhancement (RIFE) [5]. The constrained dye mobility due to entrapment on the RNA surface is evaluated by means of all-atom molecular dynamics simulations using the exon and intron binding site (EBS1/IBS1) of a group II intron [6] as a model of an RNA tertiary contact [5]. These atomistic simulations give access to the dye-linker dynamics which are key to defining the volume accessible to the fluorophore in the context of the RNA.



Building on a refined description of the dyes, a set of *de novo* modeled RNA structures is then filtered against experimentally derived distance distributions of one or multiple FRET pairs. Imposing such restraints on different parts of the RNA confines the search space while at the same time pinpointing regions of increased flexibility. We validate this integrative modeling approach by reconstituting the solution structure of the EBS1 hairpin motif *in silico*. After all, the combination of smFRET and molecular modeling will open up new avenues to explore the world of long non-coding RNAs whose three-dimensional fold is yet to be discovered.

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A Proof-of-Concept for a Photoinitiated Single-Molecule Circuit

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The ‘holy-grail’ of molecular electronics is the ability to develop fully-integrated molecular circuitry, and by extension, single-molecule circuitry.[1,2] The design principles for a molecular wire have already been well established,[3] but a molecular circuit represents a far greater challenge. A molecular wire must have charge transfer between two stations/electrodes, whereas a molecular circuit must have charge travel unidirectionally in a complete circuit and recombine at the origin. A molecular circuit also requires a controllable external field to initiate the flow of charge.

This presentation shall cover the design principles and spectroscopic characterisation of an electron donor-acceptor-acceptor (D-A-A) triad as a proof-of-concept photoinitiated molecular circuit (**Figure 1**), with a conservatively estimated quantum efficiency of 7.8%. This is achieved through three sequential charge-transfer processes, and the exploitation of geometric rearrangement in the excited state.

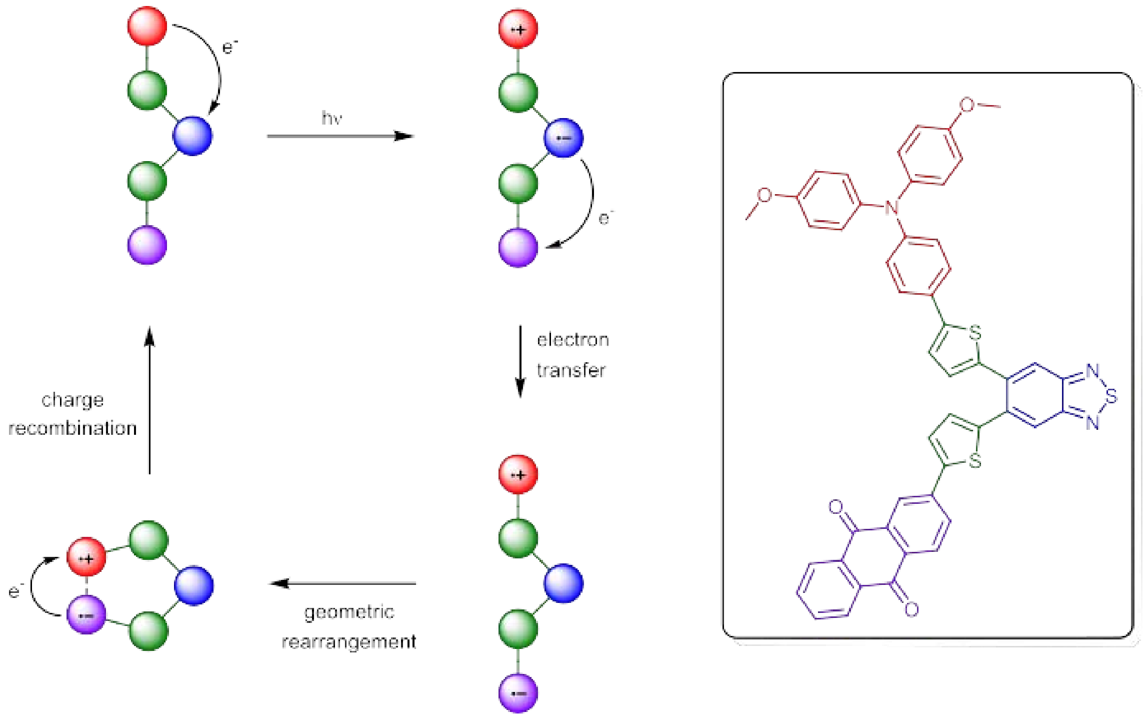

Figure 1. Proposed mechanism for the photoinitiated molecular circuit. Red = Donor, Blue = Acceptor 1, Purple = Acceptor 2, Green = Bridge.

[1] Sriharsha V. Aradhya, Latha Venkataraman, *Nature Nanotechnology*, **2013**, 8, 399-410

[2] Timothy A. Su, Madhav Neupane, Michasel L. Steigerwald, Latha Venkataraman, Colin Nuckolls, *Natrue Review Materials*, **2016**, 1, 1-15

[3] Annie Butler Ricks, Kristen E. Brown, Matthias Wenninger, Steven D. Karlen, Yuri A. Berlin, Dick T. Co, Michael R. Wasielewski, *Journal of the American Chemical Society*, **2012**, 134, 4581-4588