

Energy and electron transfer dynamics in complex organic donor-acceptor systems: project report

Grantee

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Host

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Introduction

Organic devices such as organic light emitting diodes (OLEDs) and organic solar cells constitute an important field of research. While organic materials have been used to construct functioning OLEDs and solar cells, the efficiencies of these devices still need optimization. Therefore, we need a detailed understanding of the basic processes of energy and electron transfer in such materials.

This is where we want to contribute with our work. Whether certain materials are suitable for optoelectronic applications is determined by the details of the energy and electron transfer processes between their molecular subunits. These processes are based on the interactions of the electronic systems of each component.

In this project, we analyze bichromophoric model systems in which a donor (D) moiety is covalently linked to an acceptor (A) via a bridging unit (B). In the following,

we will refer to these systems as DBAs, see Fig. 1. Light energy is absorbed by the donor and then transferred to the acceptor. This process may be accompanied by electron transfer processes in either direction.

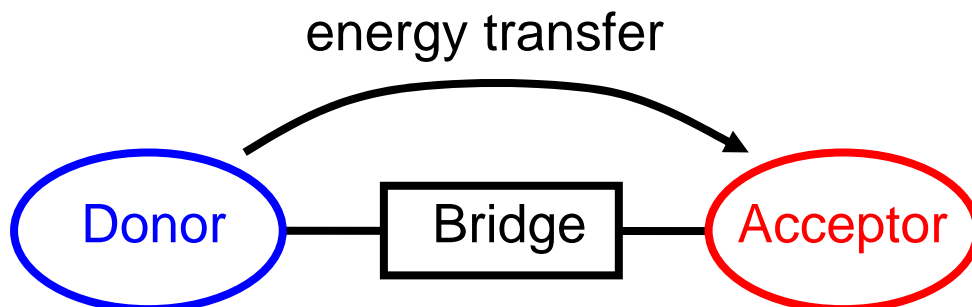


Fig. 1: Schematic view of donor-bridge-acceptor (DBA) systems.

The goal of our work is to find out which parameters influence these transport processes.

Purpose of the visit

In Bayreuth, we had already studied different DBA systems by time-resolved emission spectroscopy. Those measurements helped us characterize the energy transfer between the donor and the acceptor moiety as a function of the bridge unit and the solvent [1] [2].

The purpose of the visit to London was to investigate possible electron transfer processes in the dyads by transient absorption spectroscopy.

Description of the work carried out during the visit

Materials

All compounds have been synthesized by the group of Prof. Dr. M. Thelakkat from the department of Applied Functional Polymers at the University of Bayreuth [3] [4].

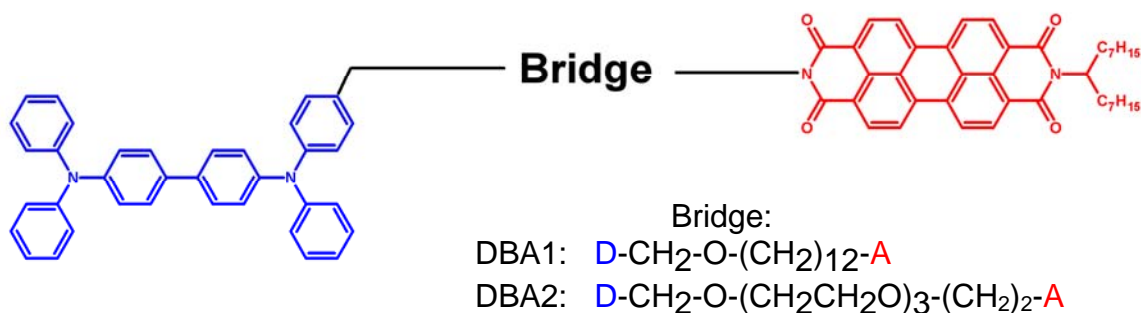


Fig. 2: The investigated tetraphenylbenzidine (donor) - perylene bisimide (acceptor) dyads.

Fig. 2 shows the two different DBA systems that were investigated in this work. Tetraphenylbenzidine (TPD) donors are covalently linked to perylene bisimide (PBI) acceptors by two different kinds of bridges. The ethylene glycol bridge of DBA2 is of approximately the same length as the alkyl bridge of DBA1, but has a different polarity.

All measurements were conducted in solution. The following solvents were used: toluene (nonpolar), acetone and ethanol (both polar).

Techniques and experimental setup:

a) Steady-state spectroscopy

Steady-state absorption and emission spectra were recorded on a Shimadzu UV_1601 UV-visible Spectrophotometer and on a Horiba Jobin Yvon Fluorolog spectrometer, respectively.

b) Transient absorption spectroscopy

The time resolved experiments were carried out by transient absorption spectroscopy (TAS). In this technique, the sample is excited by an intensive laser pulse, called the pump pulse. Right after irradiation, the chromophores are in an excited electronic

state. This excited state is not stable but will either decay to the ground state or it will undergo processes leading to the formation of new transient states. TAS now makes use of the fact that a molecule in an electronic state different from the ground state has a different absorption spectrum than an identical molecule in the electronic ground state. The absorbance of the sample in a transient state can be monitored by irradiation with a low-intensity probe beam after the initial excitation with the pump pulse. In this work, a continuous emitter was used as probe beam. Another variation of TAS uses pulsed light sources for both pumping and probing.

Generally, two kinds of experiment can be performed with this technique. In the first type, the wavelengths of both pump and probe light are fixed, although they need not be identical. The difference in absorbance between the initial state and the transient state is then recorded over time. From the resulting time trace one obtains information on the rates with which transient states are formed and on the lifetimes of those states. In the second type of experiment a fixed time delay after the pump pulse is set at which the transient signal is monitored. Then the wavelength of the probe light is varied, and so a spectrum of the transient species is obtained.

In this work, a pulsed nitrogen laser emitting at a wavelength of 330 nm was used as pump laser, while a lamp with a continuous emission spectrum served as source for the probe light. Wavelength selection of the probe light was performed by a monochromator. A second monochromator after the sample ensured that only light with the desired wavelength was recorded by the detector. Time traces were obtained by comparing the time-dependent absorption of the sample after the pump pulse both with and without the probe light. In order to evaluate transient signals with lifetimes of different magnitudes with a satisfying time resolution, time traces could be recorded in different time windows after excitation (1 μ s, 10 μ s, 100 μ s, 1 ms and 10 ms).

Results:

a) Steady-state spectroscopy

The steady-state absorption and emission spectra of 10^{-6} M DBA1 and DBA2 solutions in toluene are given in fig. 3, as well as the corresponding spectra of their constituents TPD and PBI.

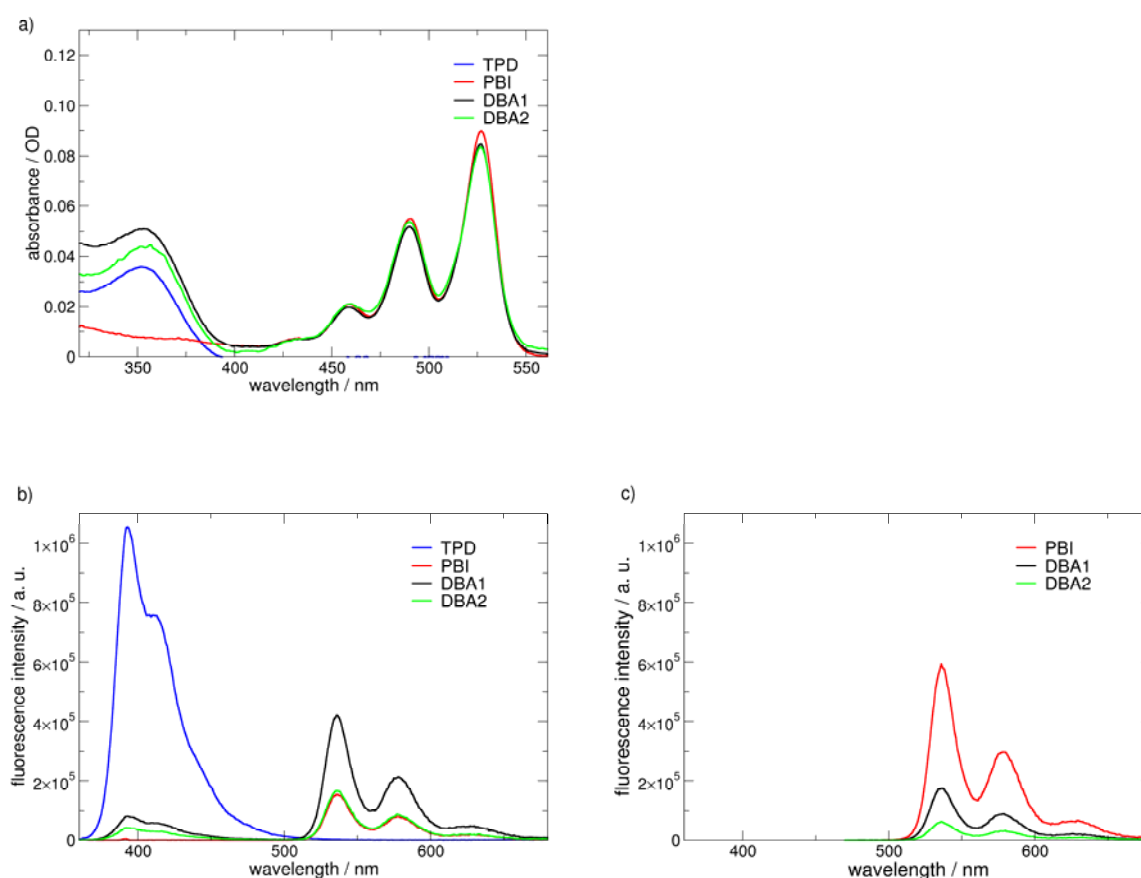


Fig. 3: Steady-state spectra of the dyads DBA1 and DBA2 and their constituents TPD and PBI in toluene ($c = 10^{-6}$ M): a) absorption, b) emission (excitation wavelength 350 nm), c) emission (excitation wavelength 460 nm)

In this work, one of the main objectives was to explain the lower fluorescence intensity (and lifetime) of PBI in the DBA molecules when directly excited (excitation wavelength $\lambda > 400$ nm) (fig. 3 c).

b) Transient absorption spectroscopy

General comments

As shown in fig. 3 above, TPD emits between 370 nm and 500 nm, and PBI between 530 nm and 700 nm. Pump-probe experiments at these wavelengths will therefore lead to stimulated emission and thus to a negative transient absorption signal in small time windows. Also, as long as the molecules are in a transient state, the absorption of the ground state will be weaker than in an unexcited sample, i. e. a negative TAS signal (bleach) will be detected with a shape corresponding to the steady-state absorption spectrum. Positive transient signals can be ascribed to the absorption of transient states formed after the pump pulse.

DBA1 in toluene

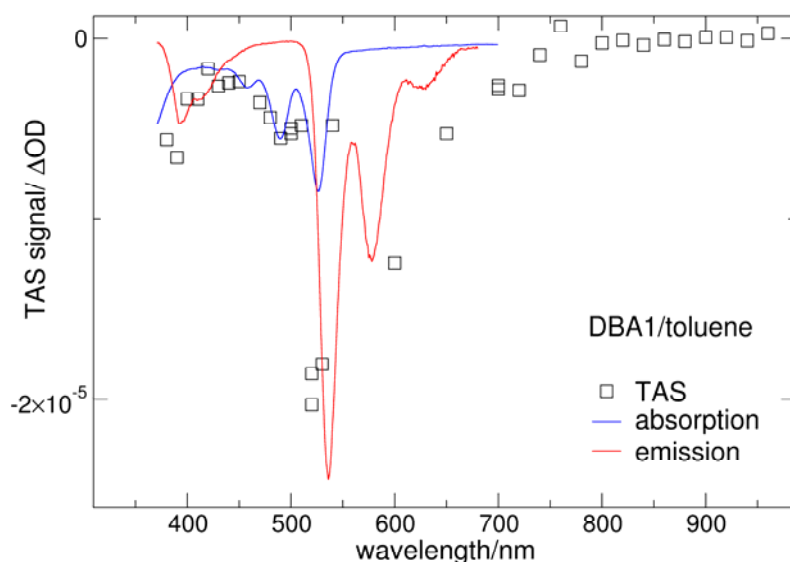


Fig. 4: Transient spectrum (open squares) of DBA1 in toluene ($c = 10^{-5} M$). The steady-state absorption (blue) and emission (red) spectra are scaled to match the TAS spectrum at 490 nm and 530 nm, respectively.

Fig. 4 shows the transient absorption spectrum of DBA1 in the nonpolar solvent toluene ($c = 10^{-5}$ M). Between 380 nm and 720 nm, negative transient signals were detected. Positive transient signals cannot be identified anywhere between 380 nm and 960 nm. The shape of the spectrum resembles a combination of the steady-state absorption and emission spectra (solid lines in fig. 4).

DBA2 in toluene

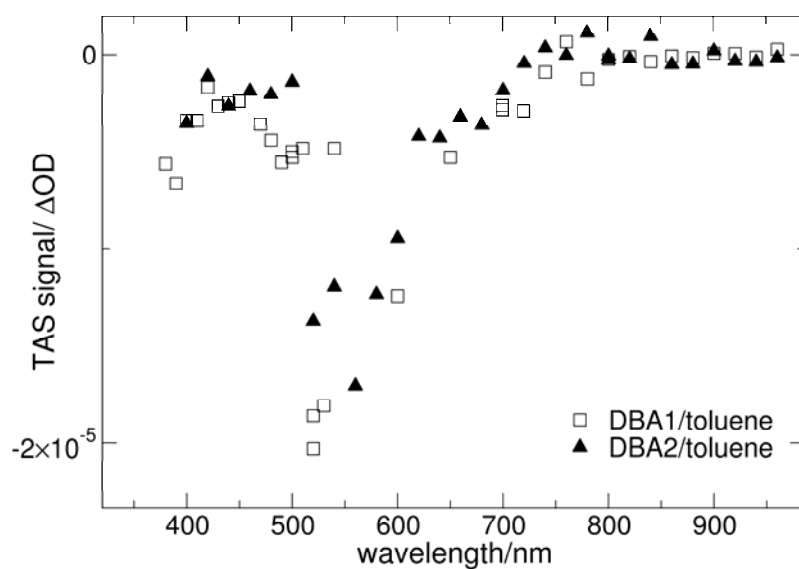


Fig. 5: TAS spectra of DBA1 (open squares) and DBA2 (filled triangles) in toluene ($c = 10^{-5}$ M).

The TAS spectrum of DBA2 in toluene ($c = 10^{-5}$ M, fig. 5) shows similar features as the TAS spectrum of DBA1 in the same solvent. Again, no significant positive TAS signals could be detected between 380 nm and 960 nm.

DBA1 in acetone

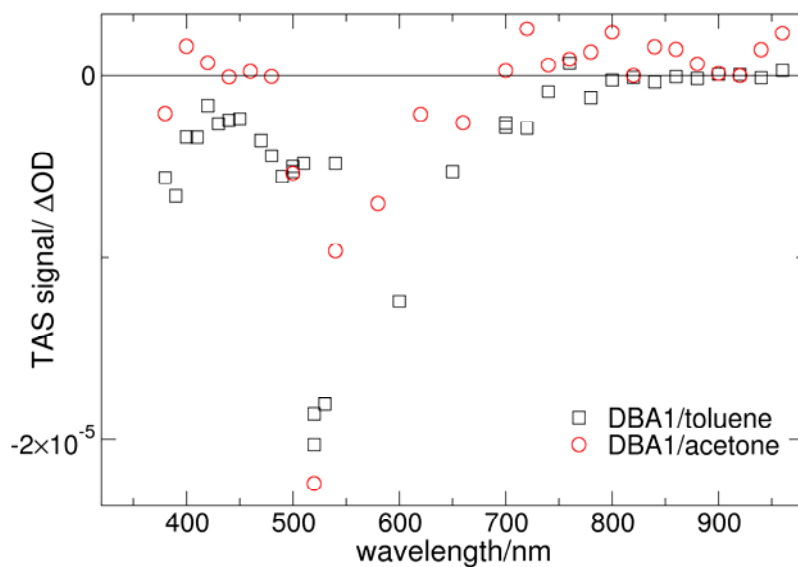


Fig. 6: TAS spectra of DBA1 in toluene (black squares) and acetone (red circles) ($c = 10^{-5} \text{ M}$).

In fig. 6 we see the TAS spectrum of DBA1 in the polar solvent acetone ($c = 10^{-5} \text{ M}$). While the negative TAS signals are still present, there are also differences to DBA1 in toluene: Between 400 nm and 480 nm, the TAS spectrum is shifted toward the zero axis, and for wavelengths $> 700 \text{ nm}$, slightly positive values were measured. While their presence can hardly be neglected, the shape of the positive part of the spectrum is still obscured by the wide scatter of the data points and therefore a clear identification of spectral bands does not seem feasible.

DBA2 in acetone

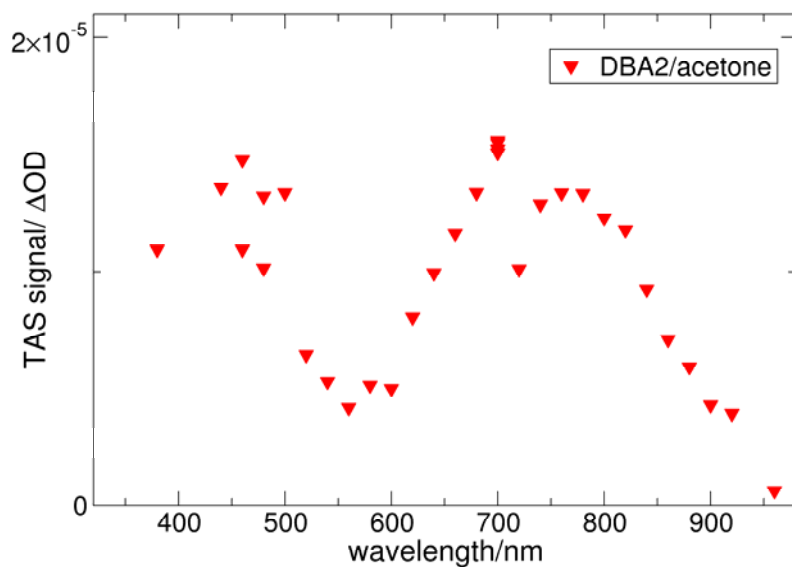


Fig. 7: TAS spectrum of DBA2 in acetone ($c = 10^{-5} M$).

In this sample, the lifetime of the observed transient state (see below) was long enough to record the transient spectrum in the time window 1 ms and thus avoid the low signal-to-noise ratio observed in the shorter time windows. Furthermore, the effects of stimulated emission can be neglected in this time window.

DBA2 in ethanol

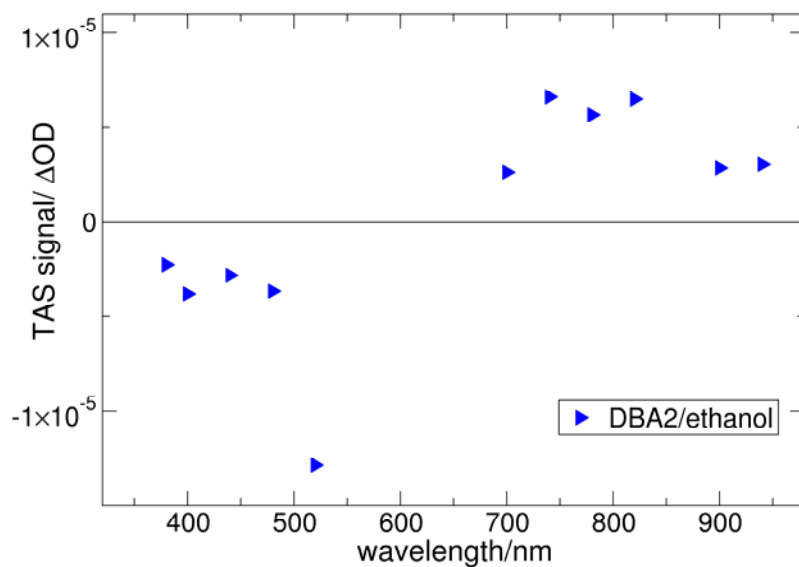


Fig. 8: TAS spectrum of DBA2 in ethanol ($c = 10^{-5}$ M).

In ethanol, the TAS-spectrum of DBA2 combines features we have already observed in other solvents (fig. 8, $c = 10^{-5}$ M). There is a bleach for wavelengths between 380 nm and 520 nm. This part of the spectrum resembles the spectrum obtained in toluene. Furthermore, there is a positive signal for wavelengths > 700 nm which resembles the spectrum in acetone, apart from the fact that the distinctive maximum at 700 nm is missing. However, the lifetime of the positive signal in this sample is too short to neglect the influence of the stimulated emission of perylenebisimide (see below) which may still play a role at this wavelength.

Dynamics/time traces

A comparison of the decay dynamics of the positive bands observed for DBA2 in the two solvents acetone and ethanol reveals an interesting behaviour.

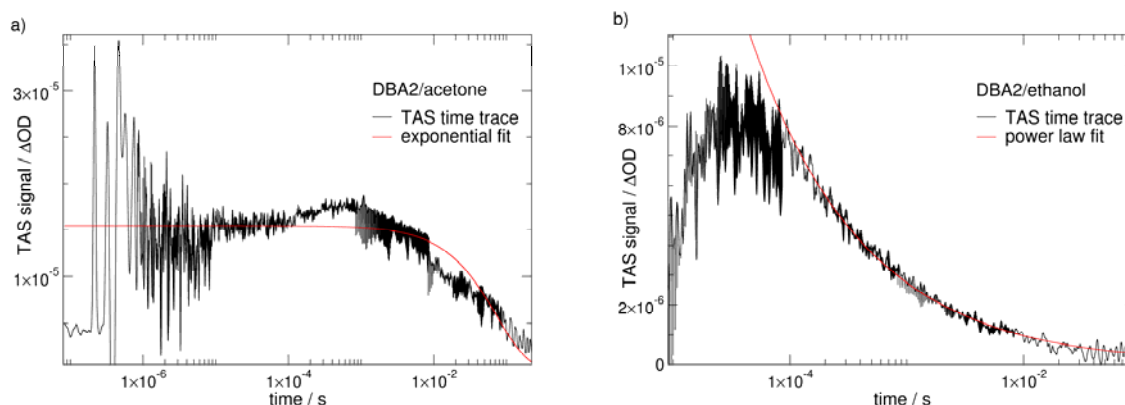


Fig. 9: TAS time traces (black) and fit curves (red) of DBA2 a) in acetone at 700 nm and b) in ethanol at 740 nm ($c = 10^{-5}$ M).

The decay curve for DBA2 in acetone at a probe wavelength of 700 nm is shown in fig. 9 a. An exponential fit model, $\Delta OD(t) = A \cdot \exp(-t/\tau)$, results in a lifetime $\tau = 74$ ms. A multiexponential fit model does not improve the fit.

In ethanol, the time trace looks different, see fig. 9 b (probe wavelength 740 nm). An exponential fit (monoexponential or multiexponential) does not describe the data satisfactorily. A power law fit model $\Delta OD(t) = B \cdot t^{-c}$ yields good fit results for the signal decay, with $c = 0.45$.

A power law fit was also tested as a possible fit model for DBA2 in acetone, yet without success. A complete time trace of DBA2 in acetone at 740 nm has not been measured, yet a comparison of the TAS traces in the time window between 10^{-4} s and 10^{-2} s after the pump pulse at the wavelengths 700 nm and 740 nm indicates the same decay kinetics at both wavelengths.

Conclusions:

Quenching of the PBI fluorescence occurs in both dyads and in all of the solvents investigated in this work. Therefore we expected to identify a unique process that is responsible for this effect. Transient absorption spectroscopy provides us with tools to identify absorption bands of any new transient species that might form after excitation of the sample.

Only the samples in polar solvents featured positive transient absorption signals between 380 nm and 960 nm. The positive signals found for DBA2 in acetone and ethanol resemble the radical ion spectra of TPD⁺ and PBI⁻ published in the literature [5][6]. For DBA1 in acetone, the signals were too weak to support a detailed analysis.

In the samples dissolved in the nonpolar toluene, no formation of new transient states that absorb between 380 nm and 960 nm could be verified. Due to the high scatter of the data, TAS signals with $\Delta OD < 10^{-6}$ could not be interpreted. Thus, the formation of transient states with a low yield below detection sensitivity cannot be ruled out completely for these samples.

The transient states of DBA2 formed in acetone and ethanol were found to follow different decay dynamics.

Future collaborations:

Future collaborations between the two groups in Bayreuth and London are under discussion because of our similar research interests and complementary equipment.

Projected publications:

We are planning to include the experimental results from this visit into one of our future publications on the subject.

Acknowledgements:

The grantee thanks the European Science Foundation (ESF) and the Elite Network of Bavaria (ENB) for their support.

Comments:

The duration of the visit was 11 weeks rather than 13 weeks as originally planned, due to unforeseeable circumstances (a death in the family).

References

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