Characterizing the functional dynamics of zinc phthalocyanine from femtoseconds to nanoseconds

Janne Savolainen a,*, Dennis van der Linden a, Niels Dijkhuizen a, Jennifer L. Herek a,b, *

a FOM Institute for Atomic and Molecular Physics (AMOLF), Kruislaan 407, 1098 SJ Amsterdam, The Netherlands
b Optical Sciences Group, Department of Science and Technology, MESA+Institute for Nanotechnology, University of Twente, Enschede 7500 AE, The Netherlands

Received 9 August 2007; received in revised form 20 November 2007; accepted 22 November 2007
Available online 16 January 2008

Abstract

A promising photosensitizer, zinc phthalocyanine, is investigated by means of steady-state and time-resolved pump-probe spectroscopies. Spectrally resolved pump-probe data are recorded on time scales ranging from femtoseconds to nanoseconds. Global analysis yields the excited-state absorption spectra and lifetimes, as well as the pathways and efficiencies of the competing relaxation processes from the initially excited S1 state. In addition to the expected nanosecond-scale processes of fluorescence, internal conversion and inter-system crossing that follow the generally accepted kinetic scheme, we also resolve ultrafast dynamics. The nature of these fast processes and their implications to the functional pathway involving triplet formation are discussed.

Keywords: Photosensitizer; Ultrafast dynamics; Energy-flow diagram; Triplet yield; Zinc phthalocyanine

1. Introduction

The functionality of photosensitizer molecules arises from their ability to react with molecular oxygen to produce highly reactive singlet oxygen and other radical species. Among the applications are photodynamic therapy, blood sterilization and sunlight activated herbicides and insecticides [1,2]. A good photosensitizer should have a high absorption cross-section at a wavelength suitable for the application, e.g. the optical window of tissue in photodynamic therapy [3]. Singlet oxygen species are created by the interaction between a photosensitizer in its triplet state and oxygen molecule, hence the quantum yield of the triplet state is a key factor when searching for or designing new photosensitizers. Other important factors include the rate of photodegradation, solubility, and the tendency to aggregate [3].

In the end, the efficiency of all these applications depends on the photophysics of the photosensitizer molecule. Improving the photosensitizer to enhance the functional pathway and suppress loss channels is an attractive route to explore by coherent control experiments using shaped ultrafast laser pulses [4]. In this approach, an optimisation experiment is designed with the goal of finding a pulse shape that will improve the yield of a chosen photophysical process in comparison to that obtained with a transform-limited (i.e. unshaped) laser pulse. Improving the triplet yield, and correspondingly the efficiency of the photosensitizer molecule in generating singlet oxygen, is a clear target for an optimisation experiments on photosensitizers. However, prior to these experiments a detailed understanding of photophysical processes involved in the excited-state deactivation, as well as their manifestation to the transient spectral signals used as feedback in the control experiments, must be acquired. Here, we report transient absorption experiments and detailed global analysis to extract the pathways, spectral signatures and efficiencies of energy flow in a prototype photosensitizer molecule.

Amongst the most promising second-generation photosensitizers for photodynamic therapy (PDT) are the phthalocyanines [1]. In this study, zinc phthalocyanine (ZnPc) is chosen to serve as a model photosensitizer to study the efficiency of the triplet yield as well as other processes occurring after the initial excitation of the chromophore (see Fig. 1). ZnPc has been in clinical trials [5,6], is easy to obtain, stable, produces singlet oxygen with
The authors report rate constants of 9.1, 38.5, and 5.6 ns, with corresponding quantum yields of 0.34 ± 0.03, 0.08 ± 0.11 and 0.58 ± 0.08 for F, IC and ISC, respectively. However, as an example of the wide variation in the reported nanosecond dynamics, we note a study by Frackowiak et al. These authors found the quantum yield for the inter-system crossing to be even as high as 0.98 ± 0.18 for ZnPc in air-saturated DMSO [12], using a photothermal measurement technique.

The triplet-state lifetime (\( \tau_T \)) is strongly affected by the presence of molecular oxygen, which drastically reduces \( \tau_T \) due to efficient intermolecular energy transfer. Grofscik et al. [9] find a \( \tau_T \) of 220 ± 22 ns for ZnPc in air-saturated ethanol; Lang et al. [22] report 1.6 \( \mu \)s for ZnPcS3 in aerated aqueous protein solution and 205 \( \mu \)s without the presence of oxygen.

In addition to the nanosecond dynamics described above, also femtosecond and picosecond processes have been reported. The S1 lifetime of ZnPc in toluene is claimed to be approximately 35 ps by Rao and co-workers, a value obtained by degenerate four-wave mixing using incoherent light [13]. The setup used, however, was inadequate for quantifying components exceeding 100 ps. In addition, the authors report a \( \sim 3.5 \) ps component that is assigned to vibrational relaxation in the S1 state, as well as a \( S_n \) dephasing time of \( <170 \) fs. Howe and Zhang report an S1 lifetime of \( \sim 160 \) ps and an S2 lifetime of \( \sim 10 \) ps for tetrasulfoned ZnPcS4 in DMSO [10]. The data were obtained by femtosecond pump-probe measurements, where excitation was to the second excited state. In explaining the multi-exponential behaviour of the kinetics, authors introduce an energy-flow model that includes an uphill climb from S1 to the S2 state at room temperature and an inverse saturable absorber model. Recently, in a study of artificial light-harvesting complexes where ZnPc is covalently linked to a carotenoid molecule, ultrafast branching of the energy flow in the singlet manifold with time scale of <100 fs has been reported by Berera et al. [24].

Collectively, the various observations from the ultrafast studies suggest that the conventional energy-flow model (Eq. (1)) fails to depict the entire picture of the kinetics, and that faster processes may also play an important role in the photophysics of ZnPc and its derivatives. However, the previous results from the ultrafast studies performed on ZnPc in solution are extremely divergent, and motivate further studies in order to resolve the intramolecular dynamics of this system.

Here, we employ pump-probe spectroscopy from femtosecond to nanosecond time scales in order to deliver a more consistent picture of the kinetic processes following the excitation of the photosensitizer. Using a state-of-the-art pump-probe setup and global analysis of the spectrally broad data we focus on the intramolecular dynamics of ZnPc in DMSO, determining the excited-state spectra, deactivation pathways, time constants and efficiencies. Besides resolving the nanosecond-scale dynamics that follow the conventional energy-level scheme, we show that there indeed are ultrafast processes present. In this context, we also address the role of the solvent, and how solvation dynamics may complicate the analysis of dynamics on ultrafast time scales [25–30]. Global analysis of the temporally and spectrally resolved data allows us to extract a complete picture of the branching ratios between the three competing intramolecular processes.
energy-flow pathways as well as the species-associated spectra (SAS). We present an energy-flow model used in the analysis and discuss the origins of all observed dynamics.

2. Experimental

Steady-state absorbance spectra were measured with a Jasco V-530 spectrophotometer, with the sample in a 1 mm quartz cuvette (Hellma). For the fluorescence measurements, a Jobin Yvon Spex Fluorolog Tau-3 system was used. The fluorescence spectrum and quantum yield were measured by the ratio method [31] using chlorophyll-a in water as a reference sample. Fluorescence lifetimes were measured in the frequency domain using the modulation technique as described in Ref. [32]. Fitting software supplied by the manufacturer was used to obtain the fluorescence lifetime.

The pump-probe setup was as follows: part of the output of an amplified Ti:Sapphire laser (Clark CPA-2001) was coupled into a non-collinear optical parametric amplifier (NOPA), which produced $\sim 10 \mu J$ near-transform-limited pulses at 672 nm with $\sim 30$ nm FWHM and 22 fs pulse duration (pump pulses). A small fraction of the residual fundamental light was focused to a 2 mm sapphire window to create a white light continuum (WLC) that provided spectrally broad probe pulses ranging from 450 to 710 nm. To avoid any anisotropy effects, the polarization angle between the pump and the probe pulses was set to 54.7°. The two beams were focused and overlapped at the sample position, where the FWHM of the Gaussian intensity profile of the pump beam was 250 μm. The pulse energy was set to 50 nJ with an adjustable filter, giving a peak power of $3.4 \times 10^{9}$ W cm$^{-2}$ ($3.4 \times 10^{14}$ photons cm$^{-2}$). The sample was circulated in a 1 mm quartz flow-cell to provide a fresh sample for every pulse to avoid sample degradation or accumulation of long-living states. The probe pulses were coupled into a 35-cm spectrograph with a 256-pixels diode array providing a resolution of $\sim 1$ nm/pixel. Diode signals were read out and AD converted at a rate of 1 kHz to get shot-to-shot statistics.

The time resolution of the pump-probe experiments as well as the amount of spectral dispersion in the WLC was determined by measuring the sum-frequency-mixing signal of the pump and probe pulses at the sample position in a 25 μm thick BBO crystal. The wavelength to be mixed from white light continuum was selected by tuning the phase matching angle of the crystal; in this way, the mixing of different wavelengths of the WLC could be measured. The time resolution was $\sim 70$ fs across the spectrum, and the overall time delay between the blue and red parts of the WLC spectrum (chirp) was approximately $\sim 300$ fs. The measured chirp curve was used to remove the WLC dispersion from the data prior to analysis.

ZnPc and DMSO were both purchased from Sigma–Aldrich and used without further purification. The optical density used in the pump-probe experiments was 0.3 at 672 nm [33], as well as a vibrational progression to the blue side with a shoulder at 645 nm and a small peak at 606 nm. The shape of the Q-band spectrum and the positions of the absorption maxima indicate that the ZnPc sample is in a monomeric form $\lambda_{\text{max}} = 345$ nm, which we label the $S_0 \rightarrow S_2$ transition.

3. Results

3.1. Steady-state and fluorescence measurements

The steady-state absorbance spectrum of ZnPc in DMSO is shown in Fig. 1. The Q-band ($S_0 \rightarrow S_1$) has a sharp maximum at 672 nm [33], as well as a vibrational progression to the blue side with a shoulder at 645 nm and a small peak at 606 nm. The shape of the Q-band spectrum and the positions of the absorption maxima indicate that the ZnPc sample is in a monomeric form [18]. Further in the ultraviolet, the Soret or B-band can be seen ($\lambda_{\text{max}} = 345$ nm), which we label the $S_0 \rightarrow S_2$ transition.
The fluorescence spectrum (Fig. 1, $\lambda_{ex} = 660$ nm) shows an almost perfect mirror image of the absorption spectrum in the Q-band region, including the vibrational progression. The maximum of emission at 680 nm corresponds to an 8 nm Stokes shift. The fluorescence quantum yield was determined to be $0.34 \pm 0.2$. Retrieval of the lifetime components, according to the modulation technique used [32], returned only one $3.4 \pm 0.2$ ns component with substantial amplitude.

3.2. Time-resolved spectroscopy

The 2D-transient surface (Fig. 2) features broad positive excited-state absorption (ESA) bands, superimposed with a deep negative signal, due to the ground-state bleach and stimulated emission (SE). These signals are identified in Fig. 2 where they are most pronounced as Bleach + SE ($A$), $S_1 \rightarrow S_{n1}$ ESA ($B_1$), $S_1 \rightarrow S_{n2}$ ESA ($B_2$), and $T_1 \rightarrow T_n$ ESA ($C$).

Directly upon excitation, an instantaneous bleach is present, as well as other overlapping signals. The negative band originally centred at 672 nm broadens and the centre of mass moves towards the red. This behaviour is explained by a dynamic Stokes shift: the solvent molecules redistribute in response to the new electron distribution in the excited state of ZnPc, which lowers the energy of this state and correspondingly red shifts the SE signal. These dynamics are more clearly demonstrated in Fig. 3 (right panel), where transient traces show a rapidly decaying negative signal on the blue side of the band (668 nm) and rapidly growing negative signal on the red side of the peak of the bleach band (686 nm). The decay is found to be bi-exponential and is fitted with time constants of $250 \pm 30$ fs and $2.5 \pm 0.2$ ps.

Further ultrafast dynamics can be resolved in other regions of the transient absorption spectrum (Fig. 3, left panel). The initial decays of the ESA bands in the spectral regions 460–490 and 615–645 nm are mono-exponential and can be fitted with a time constant of $450 \pm 50$ and $250 \pm 30$ fs, respectively. Likewise, the trace at 532 nm requires a $250 \pm 30$ fs component, but here with a negative pre-exponential factor (i.e. a rise).

In the later time window extending to nanoseconds, the dominating negative bleach band narrows and the centre of mass moves towards the blue, ultimately reaching perfect overlap with the steady-state spectrum ($\lambda_{max} = 672$ nm). The ESA band at $\sim 630$ nm decays completely, while below 500 nm the signal persists. Careful inspection of this region shows that maximum, however, is shifted. In Fig. 4, spectral cross-sections reveal that at 7 ps the ESA band on the blue edge of the spectrum has its maximum at 486 nm, while at 7 ns the band peaks at 480 nm. Accounting for the effective fluorescence lifetime (the lifetime of the $S_1$ state) of $2.9 \pm 0.2$ ns, and the fact that ISC process must occur on the same time scales to allow for a significant triplet quantum yield, we assign the band in the early time window to the $S_1 \rightarrow S_{n1}$ ESA and the band at later times to the $T_1 \rightarrow T_{n1}$ ESA. Time evolution in this time window across the measured spectrum is shown by time traces at selected wavelengths (Fig. 4, inset).

The late time window of the 2D surface (from 7 ps to 7 ns) can be well fitted according the kinetic model corresponding to...
equation 1, in which three competing processes (F, IC and ISC) account for the deactivation of the S\textsubscript{1} state. The resulting SAS are shown in Fig. 5 and quantum yields and lifetimes are given in Table 1. Note that in the global fitting, the depopulation of S\textsubscript{1} is described by two pathways with rate constants K\textsubscript{ISC} and (K\textsubscript{IC} + K\textsubscript{F}). Hence, in order to resolve all three quantum yields we make use of Eq. (1), the separately determined fluorescence quantum yield [34], and the following three equations:

\[
k_F = \frac{\Phi_F}{\tau_F},
\]
\[
k_{ISC} = \frac{\Phi_F}{\tau_F} \frac{1}{\tau_F},
\]
\[
k_{IC} = \frac{1 - (\Phi_F - \Phi_T)}{\tau_F},
\]

where \(k_F\) is the measured fluorescence rate constant and \(k_{ISC}\) and \(k_{IC}\) are the rate constants of inter-system crossing and internal conversion, respectively.

From the SAS (Fig. 5) it is clear that the ESA bands are very broad and also overlap the bleach/SE signals. The ESA in the singlet manifold shows two distinct bands peaking around 490 and 640 nm, whereas the triplet ESA has only one clear maximum at about 480 nm. This difference explains the shift of the maximum of the ESA signal in the blue region of the measured spectrum, which is due to the decay of population in the S\textsubscript{1} state, concurrent with the population growth in the T\textsubscript{1} state. The 2.8 ns lifetime of the S\textsubscript{1} state determined from the fit matches well with previous studies [6,15,34], and the effective fluorescence lifetime measured in this study. The position found for the SE spectrum is red shifted by 8 nm, with respect to the peak of the bleach (672 nm), congruent with the Stokes shift found in the steady-state fluorescence measurements. Furthermore, the strong negative signal is first broadened on the red side due to SE and then narrows to the width given by the pure bleach signal when S\textsubscript{1} state is fully depleted.

The ultrafast dynamics observed in the first few picoseconds depict additional processes that cannot be accounted for with such a simple kinetic scheme. Hence, accurate modelling requires a more elaborate description. Bearing in mind that the measured data is a superposition of overlapping signals and that the bleach signal occurs instantaneously, the ultrafast evolution of the transient 2D-surface must be due to excited-state processes, such as energy flow between electronic states, vibrational wavepacket dynamics and/or solvation processes.

To better interpret these fast components we refined the kinetic model, as discussed in the following section.

4. Discussion

Based on our global analysis of the data, we aim to update the energy-level diagram of ZnPc. As a caveat, we note that the excited-state absorption bands are very broad and the density of states is high; hence, such a simplistic level scheme is likely inadequate in describing the real molecule in solution. This disclaimer is also important in the assignment of energies to the excited states, which are taken from the maxima of each broad transition. Nevertheless, such a model is a good basis for discussion and is useful in providing organized information, once its limitations are recognized.

The ESA signal from the S\textsubscript{1} state allows us to identify two distinct higher-lying states in the singlet manifold (S\textsubscript{n1} and S\textsubscript{n2}, see Fig. 6). S\textsubscript{n2} is accessed from the S\textsubscript{1} state with probe wavelengths in the range of 460–490 nm, and S\textsubscript{n1} in the range 615–645 nm. Taking the centre of these ESA bands, we put the energies of these levels at 35,500 and 30,800 cm\textsuperscript{-1} from the ground state. In addition, the observed ultrafast components indicate the presence of short-lived processes involved in the early time dynamics of the system. To our knowledge, these processes have not been previously reported for ZnPc. However, other molecules in DMSO have shown similar dynamics attributed to solvation processes [30].

It is well known that solvation dynamics can occur on several time scales [25–30]. For example, dielectric relaxation (i.e. the Stokes shift) generally takes place in picoseconds, while inertial components of the solvent dynamics occur on femtosecond time scales. Hence, it is no surprise that these different time scales show up also here. The solvation process is nonexponential in nature, and can be characterized only approximately by a set of exponential decay times. In a study of the solvation dynamics of coumarin 153 in DMSO [30], the spectral solvation response function could be fitted with time constants of 214 fs, 2.29 ps and 10.7 ps. The fastest component was assigned to the inertial component of solvation followed by the dielectric nature of the solvation processes. In light of this, we are inclined to attribute the 250 fs time constant, while not directly corresponding to one of the previously determined time constants for DMSO solvation dynamics [30],

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Lifetimes and quantum yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F) (IC)</td>
<td>(ISC)</td>
</tr>
<tr>
<td>QY 0.28\textsuperscript{a}</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>Lifetime/ns 10.1 ± 0.3</td>
<td>38 ± 1</td>
</tr>
</tbody>
</table>

\(\text{From Ref. [34].}\)
may also have the same origin. Alternatively, it could reflect intramolecular dynamics occurring in the ZnPc deactivation, such as relaxation or equilibration between energy levels. Likely targets would be the two degenerate Q states in ZnPc, which are spectroscopically indistinguishable upon excitation, or an independent precursor energy level that rapidly decays to the S1 state. Even though the ultrafast components can be clearly observed in the data over a wide spectral range (see Fig. 3), the fitting program was unable to extract neither unique spectral bands nor connections to other states for these features without substantial initial input and fitting restrictions. Unfortunately, the data offer no decisive evidence for assigning the 450 fs component; nonetheless, the existence of ultrafast dynamics that cannot be explained by the generally accepted energy-flow scheme is evident, and furthermore is not without precedent.

Previous studies fail to paint a clear picture of the ultrafast dynamics of ZnPc. Bearing in mind that some of these studies were on ZnPc derivatives (i.e. tetrasulfonated ZnPc), we nonetheless feel a comparison is worthwhile. Our justification is based on ab initio calculations that indicate the primary photophysics originate from the central conjugated ring structure of the ZnPc molecule [35,36].

Howe and Zhang [10] have suggested a model including an energy-flow equilibrium between S1 and S2 states in tetrasulfonated ZnPc. At room temperature, $kT$ is approximately 200 cm$^{-1}$ where as the energy separation between the S1 and S2 states is 14,100 cm$^{-1}$. Hence, we find it unlikely that a molecule in the S1 state could gain enough energy to jump to the S2 state, or that there could ever be an equilibrium between the two excited states. Furthermore, the 10 ps lifetime for the S2 $\rightarrow$ S1 inter-

Fig. 6. Schematic of the proposed new energy-level diagram for ZnPc showing both the singlet (S) and triplet (T) manifolds and the deactivation pathways from the S1 state: fluorescence, F; internal conversion, IC; intersystem crossing, ISC, and phosphorescence, Ph. Newly found states and energy spacings are shown in bold.
Finally, the possible existence of ultrafast intramolecular dynamics and branching in the deactivation of the ZnPc photosensitizer molecule opens new opportunities for coherent-control experiments \[37,38\]. In further studies, we will explore the possibility to find a laser pulse shape that leads to enhancement of the functional channel in which excitation energy flows to the triplet state. Success would further imply that it is possible to enhance the efficiency of this photosensitizer by means of pulse shaping.

5. Conclusions

We conclude that by combining fluorescence and pump-probe measurements with global analysis of the data we can describe the excited-state dynamics of ZnPc in detail. Once the fluorescence lifetime and quantum yield are known, careful transient-absorption measurements combined with global analyses provide information about the kinetics of the molecular system, ranging from femtosecond to nanosecond time scales. With this, we are able to resolve the lifetimes and quantum yields of fluorescence, internal conversion, and inter-system crossing processes, determine the species-associated spectra belonging to the excited states, and extract dynamics due to solvation. We suggest a new energy model, comprising newly resolved excited states, and extract dynamics due to solvation. We conclude that by combining fluorescence and pump-probe measurements with global analysis of the data we can describe the excited-state dynamics of ZnPc in detail. Once the fluorescence lifetime and quantum yield are known, careful transient-absorption measurements combined with global analyses provide information about the kinetics of the molecular system, ranging from femtosecond to nanosecond time scales. With this, we are able to resolve the lifetimes and quantum yields of fluorescence, internal conversion, and inter-system crossing processes, determine the species-associated spectra belonging to the excited states, and extract dynamics due to solvation. We suggest a new energy model, comprising newly resolved excited states, and extract dynamics due to solvation. We conclude that by combining fluorescence and pump-probe measurements with global analysis of the data we can describe the excited-state dynamics of ZnPc in detail. Once the fluorescence lifetime and quantum yield are known, careful transient-absorption measurements combined with global analyses provide information about the kinetics of the molecular system, ranging from femtosecond to nanosecond time scales. With this, we are able to resolve the lifetimes and quantum yields of fluorescence, internal conversion, and inter-system crossing processes, determine the species-associated spectra belonging to the excited states, and extract dynamics due to solvation. We suggest a new energy model, comprising newly resolved excited states, and extract dynamics due to solvation. We conclude that by combining fluorescence and pump-probe measurements with global analysis of the data we can describe the excited-state dynamics of ZnPc in detail. Once the fluorescence lifetime and quantum yield are known, careful transient-absorption measurements combined with global analyses provide information about the kinetics of the molecular system, ranging from femtosecond to nanosecond time scales. With this, we are able to resolve the lifetimes and quantum yields of fluorescence, internal conversion, and inter-system crossing processes, determine the species-associated spectra belonging to the excited states, and extract dynamics due to solvation. We suggest a new energy model, comprising newly resolved excited states, and extract dynamics due to solvation. We conclude that by combining fluorescence and pump-probe measurements with global analysis of the data we can describe the excited-state dynamics of ZnPc in detail. Once the fluorescence lifetime and quantum yield are known, careful transient-absorption measurements combined with global analyses provide information about the kinetics of the molecular system, ranging from femtosecond to nanosecond time scales. With this, we are able to resolve the lifetimes and quantum yields of fluorescence, internal conversion, and inter-system crossing processes, determine the species-associated spectra belonging to the excited states, and extract dynamics due to solvation. We suggest a new energy model, comprising newly resolved excited states, and extract dynamics due to solvation. We conclude that by combining fluorescence and pump-probe measurements with global analysis of the data we can describe the excited-state dynamics of ZnPc in detail. Once the fluorescence lifetime and quantum yield are known, careful transient-absorption measurements combined with global analyses provide information about the kinetics of the molecular system, ranging from femtosecond to nanosecond time scales. With this, we are able to resolve the lifetimes and quantum yields of fluorescence, internal conversion, and inter-system crossing processes, determine the species-associated spectra belonging to the excited states, and extract dynamics due to solvation. We suggest a new energy model, comprising newly resolved excited states, and extract dynamics due to solvation. We conclude that by combining fluorescence and pump-probe measurements with global analysis of the data we can describe the excited-state dynamics of ZnPc in detail. Once the fluorescence lifetime and quantum yield are known, careful transient-absorption measurements combined with global analyses provide information about the kinetics of the molecular system, ranging from femtosecond to nanosecond time scales. With this, we are able to resolve the lifetimes and quantum yields of fluorescence, internal conversion, and inter-system crossing processes, determine the species-associated spectra belonging to the excited states, and extract dynamics due to solvation. We suggest a new energy model, comprising newly resolved excited states, and extract dynamics due to solvation.

Acknowledgements

We thank Chantal de Wit, Rudi Berera, and John Kennis (Vrije Universiteit Amsterdam) for help with measurements and their insights in discussions of the data analysis. We also thank Riccardo Fanciulli (AMOLF) for his expertise in the laboratory. This work is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)”, which is financially supported by the “Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO)”. From these agencies, we acknowledge specific support via FOM Springplank and NWO-CW VIDI grants.

References