Coherent control of single molecules at room temperature

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The detection of individual molecules allows to unwrap the inhomogeneously broadened ensemble and reveal the spatial disorder and temporal dynamics of single entities. During 20 years of increasing sophistication this approach has provided valuable insights into biomolecular interactions, cellular processes, polymer dynamics, *etc.* Unfortunately the detection of fluorescence, *i.e.* incoherent spontaneous emission, has essentially kept the time resolution of the single molecule approach out of the range of ultrafast coherent processes. In parallel coherent control of quantum interferences has developed as a powerful method to study and actively steer ultrafast molecular interactions and energy conversion processes. However the degree of coherent control that can be reached in ensembles is restricted, due to the intrinsic inhomogeneity of the synchronized subset. Clearly the only way to overcome spatio-temporal disorder and achieve key control is by addressing individual units: *coherent control of single molecules.* Here we report the observation and manipulation of vibrational wave-packet interference in individual molecules at ambient conditions. We show that adapting the time and phase distribution of the optical excitation field to the dynamics of each molecule results in a superior degree of control compared to the ensemble approach. Phase reversal does invert the molecular response, confirming the control of quantum coherence. Time-phase maps show a rich diversity in excited state dynamics between different, yet chemically identical, molecules. The presented approach is promising for single-unit coherent control in multichromophoric systems. Especially the role of coherence in the energy transfer of single antenna complexes under physiological conditions is subject of great attention. Now the role of energy disorder and variation in coupling strength can be explored, beyond the inhomogeneously broadened ensemble.

1. Introduction

The detection of individual molecules is a widely applied method to discern and follow molecular photodynamics beyond the intrinsic inhomogeneities of the ensemble.[1] The applications of "single-molecule detection" stretch across all fields, from physics, to chemistry and biology: *e.g.* the nature of dark states in molecules[2] or quantum dots;[3] efficient single photon sources;[4] detection of nanoscale optical fields;[5] the dynamics of supramolecular complexes[6] and polymers;[7] DNA and protein interactions;[8] natural light harvesting systems;[9] cell membrane

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organisation[10] and intracellular processes.[11] Generally, in all these experiments the single molecular fluorescence is detected by high quantum efficiency photon counters, typically with signals of 10^3 (up to 10^6) counts per second and detector response times of 40–200 ps. As a result real-time dynamics can be recorded with sub-millisecond time resolution. Using time-correlated-single-photon-counting (TCSPC) and pulsed lasers also faster processes, such as fluorescence rates and charge transfer dynamics, can be recorded with ~100 ps time resolution, yet with integration times of milliseconds or even longer.

The dynamic range of single molecule detection is fundamentally limited by detection of the "slow" nanosecond spontaneous emission. Particularly the ultrafast fs-ps regime is a true challenge. In fact, ultrafast spectroscopy of ensembles, with methods such as transient pump–probe spectroscopy, relies on absorption detection. Detection of a single molecule in absorption, with its minute cross-section at room temperature, is an equally challenging task. Yet progress is being made. Recently single molecules were detected with photothermal contrast, *i.e.* the heating of their environments by single-molecule absorption could be detected as change in local refractive index contrast.[12] In parallel, first individual molecules were detected at room temperature in direct absorption, mainly by ultimate reduction of the background noise.[13,14] Though this technique is promising, the absorption contrast is yet very limited for ultrafast experiments. The inverse process, stimulated emission detection, is also being explored and might reach single molecule sensitivity in the near future.[15]

Several years ago we started to explore routes towards ultrafast single-molecule detection.[16] Individual molecules were excited by a delayed pulse pair, while recording the fluorescence. A femtosecond pulse exciting a molecule can at most result in *one* fluorescence photon, while the molecule will have decayed to the ground state before the next pulse arrives. Thus to make two delayed pulses interact with one and the same molecule it is imperative to operate close to saturation conditions, whereas in the linear regime only the pulse repetition rate is effectively doubled. Unfortunately a single fluorophore driven at saturation conditions will bleach very fast. By optimizing the laser repetition rate to the saturation conditions of the molecule we managed to establish workable settings and record ultrafast traces of single molecules.[17] The average photon count rate corresponded to half the laser pulse repetition rate, confirming a balance between stimulated absorption and emission: saturation indeed. At short delay times (<300 fs) we observed transients indicative of intramolecular vibrational relaxation and dephasing at room temperature. We extended the method to multichromophoric complexes, revealing the effect of conformational disorder on fs photodynamics, for the first time at the level of single complexes.[18]

From these experiments we deduced two important lessons for future research. First: exciting single molecules at saturation conditions at room temperature should be avoided, as it limits severely the time window of observation. Second: the carrier envelope offset phase of the delayed pulses should be controlled to get insight into coherent phenomena. The logical solution is: *coherent control of a single molecule*, which is the subject of this communication. The combined use of a broad band pulse and a pulse shaper allows versatile generation of pulse pair sequences by spectral modulation of one-and-the-same pulse. Such coherent experiments can be carried out in the linear excitation regime, thus relaxing substantially the conditions for single molecule detection. Moreover a pulse shaper allows for rapid electronic control of the spectral phase and amplitude, allowing phase scans before photo bleaching of the molecule.

In recent years the observation of coherences at room temperature is receiving great attention.[19–23] Particularly the discovery of long-lived electronic coherences, up to 200–300 fs, in various photosynthetic complexes (Fenna-Matthews-Olson, FMO; marine cryptophyte algae) has generated strong efforts, both in experiment and theory, to understand their origin and explore their potential role in biological function. The occurrence of coherences in pigment–protein complexes at

physiological conditions challenges the common notion that interactions with the local environment universally lead to decoherence; possibly the protein scaffolds protect electronic coherences.[21–23] Even the possibility of entanglement in light-harvesting complexes was proposed.[24–26] So far experimental approaches have concentrated on 2D-electronic-spectroscopy on ensembles of pigment-protein complexes at various temperatures. Unfortunately any observed coherence is a spatial and temporal average of an inhomogeneous distribution and therefore hard to relate to particular functionality in complex natural systems. Consequently coherent ultrafast detection of individual complexes will be important to unravel the role of coherence in the efficiency of natural photosynthetic complexes.

Here we will describe our experimental approach, illustrated with step-by-step results. The observation of vibrational wave-packets of individual organic molecules at room temperature is shown.[27] Most importantly superior coherent control is achieved by addressing an individual molecule as a well-defined single quantum system.[27,28]

2. Molecule and method

As molecule of study we used a higher rylene homologue: DiNaphtho-Quaterrylene-bis(Dicarbox-Imide)†, in short DN-QDI (Fig. 1). Rylenes are π-conjugated systems with outstanding chemical, thermal and photochemical stability, forming excellent building blocks for (excitonic) energy transfer systems. Terrylene-imides are particularly suited for single molecule studies because they exhibit high fluorescence quantum yields of 40–99% combined with good photo-stability.[29] DN-QDI has a fluorescence lifetime of about 3 ns and a quantum efficiency of 40%. Its core expansion with additional naphthalene units shifts the absorption spectrum

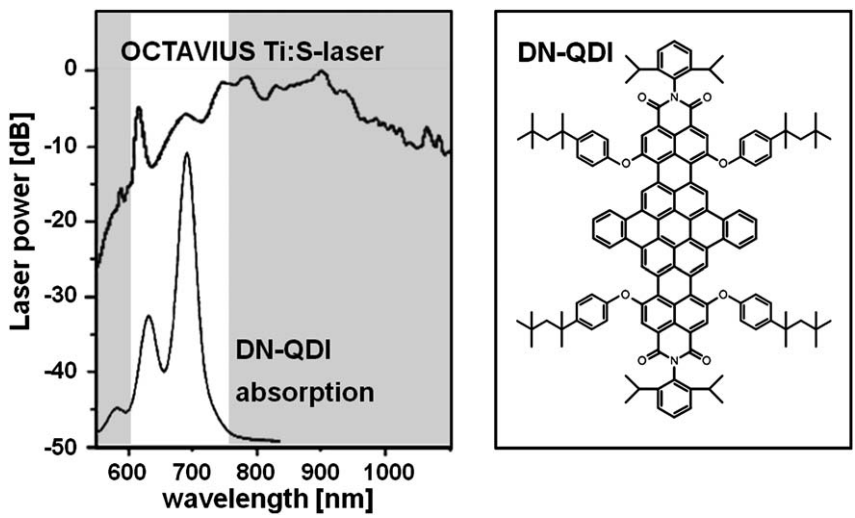

Fig. 1 (left) Broad band spectrum (log-scale) of the 7 fs Octavius Ti:Sa laser used for excitation, and absorption spectrum (linear scale) of the molecule DN-QDI, with maximum at 700 nm and clear vibrational progression; (right) molecular structure of the red fluorophore DN-QDI, DiNaphtho-Quaterrylenebis(Dicarbox-Imide)†.

† *N*,*N*9- bis-(*N*-2,6-diisopropylphenyl)-1,6,11,16-tetrakis[4-(1,1,3,3-tetramethylbutyl)-phenoxy]-8,9:18,19-dinaphthoquaterrylene-3,4:13,14-bis(dicarboximide)

to the near-infrared up to 750 nm with a maximum at 700 nm (in toluene solution).[30] It exhibits a prominent vibrational progression (C–C stretch, ~1380 cm^{-1}); see Fig. 1.

Single-molecule samples were prepared by dissolving DN-QDI together with poly (methyl-metacrylate), PMMA, in toluene and spin-coating this solution onto standard microscopy glass cover-slips. With a concentration of about 10^{-9} Molar of DN-QDI thin layers (~40 nm) were prepared with less than one molecule per μm^2.

To achieve phase control of a single molecule it is important to coherently excite a large part of the absorption band. Here we drive the molecule with the output of a 85 MHz repetition rate mode-locked Octavius Titanium:Sapphire-laser (Octavius-85M, Menlo Systems, IdestaQE[31]). The Octavius spectrum stretches from ~550 nm wavelength to deep into the infrared, spanning an "octave" in frequency, providing a 7 fs pulse when Fourier limited (Fig. 1). Here we selected a spectral bandwidth of 120 nm (15 fs) around the central wavelength of 676 nm (white band in Fig. 1), thus covering nearly the entire DN-QDI absorption spectrum, and interacting with a manifold of vibrational levels in the electronically excited state.

For coherent control we employed a 4f-pulse shaper based on a Spatial Light Modulator (SLM) for dispersion control and pulse shaping. The 4f-pulse shaper was adapted from the Multiphoton Intrapulse Interference Phase Scan (MIIPS-Box of Biophotonics Solutions Inc.).[32] The MIIPS system was modified to operate at wavelengths below 700 nm, with the second harmonic spectrum being detected in the sample plane. The shaper is designed in a double-pass configuration,[33] with a mirror at the end of the beam path reflecting the light back for a second pass through the shaper. This double-pass configuration minimises spatio-temporal coupling[34] and allows larger phase distortions to be compensated. For the experiments using 15 fs pulses and the SLM for pulse shaping, the lowest central laser wavelength with sufficient spectral intensity across the entire 120 nm band to allow for accurate phase compensation and pulse shaping was 676 nm. In all experiments pulses were first compressed to their transform limit of 15 fs in the sample plane.

3. Single molecules excited by a delayed femtosecond pulse pair

Single molecules were detected in a home-built *epi*-fluorescence confocal microscope. The shaped fs-laser light was first spatially filtered in a lens-pinhole-lens combination, directed towards the confocal microscope, and finally focussed onto the single-molecule sample with a 1.3 NA objective (Fluar, Zeiss). The excitation power was permanently recorded with a photodiode at the sample position and kept constant for all settings of the pulse shaper. The single molecular fluorescence was separated from the exciting laser light by a suitable combination of dichroic beam splitters and long-pass filters. Finally the fluorescence was split by a polarising beam splitter and tightly projected onto two, high quantum efficiency, 180 μm area, Avalanche Photo-Diodes (APD, Perkin Elmer). The two channel polarization detection gives direct insight in the orientation of the molecular emission dipole in the focal plane; moreover it provides two independent recordings on the effects of pulse shaping.

In a typical experiment the single molecule sample is scanned using a piezo-electric stage with nanometric position feedback (100 × 100 μm^2, Mad City Labs) to image the fluorescence and acquire an overview of the position of the molecules. Fig. 2 presents a 100 × 100 μm^2 image revealing many thousands of individual fluorescent molecules. Next one zooms in on a selected area of the high resolution image to identify the molecular position with nanometric accuracy. Selected single molecules are consecutively brought into the focus of the excitation beam, to record the fluorescence signal as a function of the pulse shape until photo-bleaching. Fig. 2 shows a typical time trace, with the single molecule emitting fluorescence photons during 57 s, until the discrete and irreversible photo-bleaching. In time the pulse shaper is set to generate a fs-pulse-pair with time delay increasing from 0 to 150 fs while

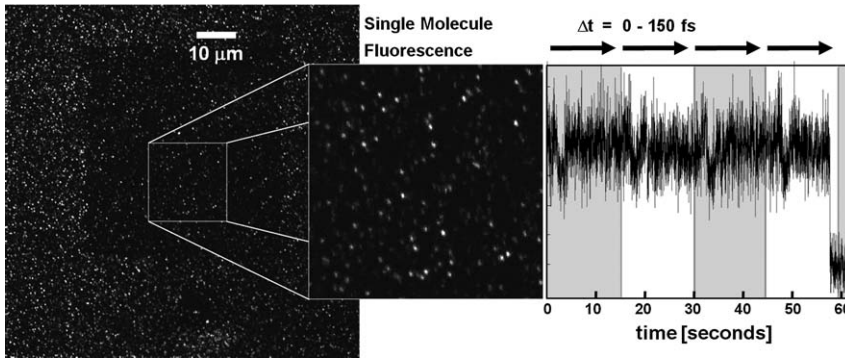

Fig. 2 (left) 100×100 μm^2 overview of an area with thousands of individual fluorescent molecules; (middle) 20×20 μm^2 detail, showing diffraction limited spots of individual molecules, with different fluorescence intensity mainly due to distinct dipole orientation; (right) time trace of a selected molecule, showing fluorescence during 57 s, until discrete photo-bleaching. The molecule was repetitively excited with a delayed double fs-pulse, with delay from 0 to 150 fs (grey-white segments). The delay scan shows as a recurring and controlled variation in the fluorescence intensity.

keeping their relative phase at zero. The pulse sequence is repeated every 15 s (grey-white segments in Fig. 2). Indeed a repetitive and reproducible response can be recognized in the molecular fluorescence signal.

This molecular response basically reflects the variation in excitation probability upon pulse shaping. Here two effects should be distinguished. On the one hand we intent to probe the temporal molecular dynamics by pulse shaping. On the other hand any change in the local excitation conditions will affect the recorded fluorescence of a molecule. To disentangle these effects we monitor the excitation intensity at the focal point. However, overall intensity control is not enough, because 4f-shaper manipulates spectral components in space and thus generally the output beam of any shaper contains spatially distributed spectral (or temporal) components.[34] To avoid spatio-temporal coupling the 4f-shaper is operated in double-pass configuration.[34] Moreover, using the MIIPS system, we make sure to start each experiment with a Fourier-limited pulse, *i.e.* flat spectral phase, in the focus of the confocal microscope.

4. Phase controlled excitation of single molecules

Complete information on both spatial and temporal response is best obtained by scanning full images at various settings of the pulse shaper. Fig. 3 shows a typical example of a set of molecules excited by a delayed pulse pair with increasing delay of $\Delta t = 0$, 21 and 42 fs. The excitation power of the pulse pair is kept constant while the carrier phase difference between each pulse pair is set zero. Diffraction limited spots (~300 nm FWHM) are observed with different fluorescence intensity, sometimes noisy due to the limited signal/noise ratio (about 10) when detecting single molecules. Upon close inspection of the different panels (0-21-42 fs) one observes molecules #1, 2 and 3 to change from dim to bright to dim. In contrast molecules #4, 5 and 6 rather change from bright to dim to bright. Similar other cases can be discerned. Finally certain molecules, such as #7, 8 and 9 show up in the first panel, but have bleached and disappeared in subsequent panels.

To obtain the underlying molecular dynamics we determine the integrated fluorescence intensity of each spot as function of the pulse pair delay. By taking the spatially integrated intensity we are sure to remove any residual spatio-temporal coupling caused by the shaper. Fig. 4a shows the fs time delay (Δt) response for

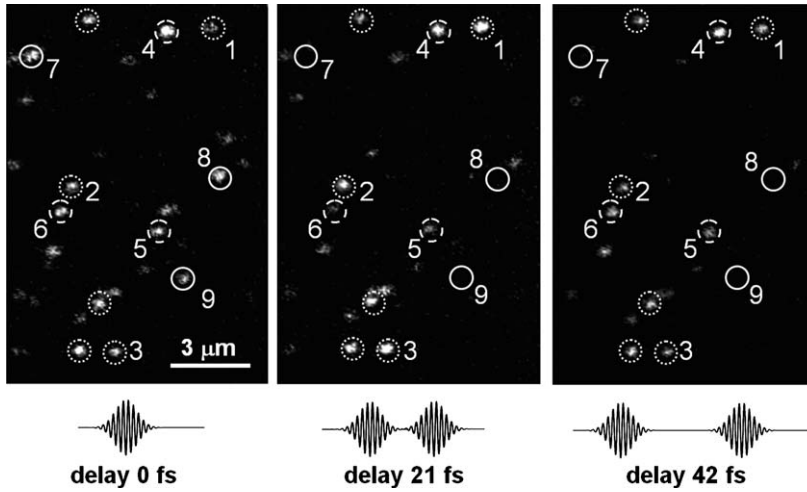

Fig. 3 Fluorescence images of a set of individual DN-QDI molecules excited by a delayed fs pulse pair with 0, 21 and 42 fs delay, respectively. Note the different response amongst molecules: molecules 1, 2 and 3 show dim-bright-dim, while molecules 4, 5 and 6 show bright-dim-bright. Molecules 7, 8, 9 bleached after the first image.

two different molecules. The relative fluorescence is normalized to the fluorescence at long time delay. The single molecule response shows strong oscillatory variations up to 50% of the average signal. The oscillations persist up to ~100 fs with a period of typically 30–40 fs. Interestingly the two presented molecules differ in phase; in fact their response is almost out of phase, for identical excitation conditions.

The oscillations are caused by wave-packet interference: constructive or destructive interference of the excited state wave packets generated by the delayed pulse pair. Fourier analysis shows a vibrational frequency typical for the carbon-carbon stretch at ~1070 cm^{-1}. The difference between the molecules reflects the structural disorder in the molecule-polymer-host system. The inhomogeneously broadened absorption spectrum (Fig. 1) is composed of many individual spectra. The specific spectral width and centre frequency of each molecule compared to the laser spectrum determines the ultrafast response. Thus the two molecules in Fig. 4a have slightly distinct absorption spectra and we are starting to unravel the inhomogeneous broadening. Clearly the average over many individual molecules, reconstituting the

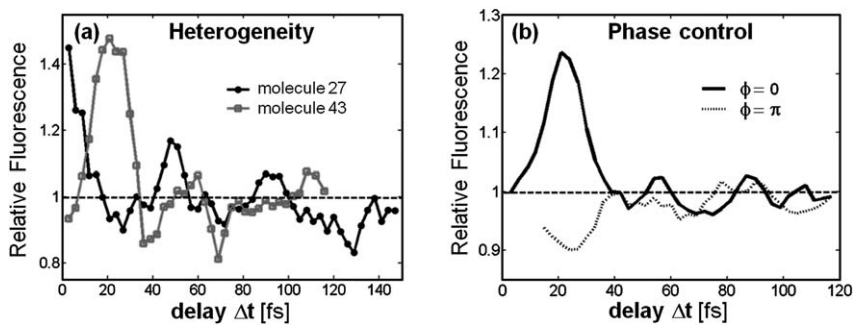

Fig. 4 (a) Integrated fluorescence as function of pulse delay Δt for two different molecules; (b) phase control of single-molecule wave packets: Single molecule fluorescence as function of pulse delay Δt for two in-phase ($\phi = 0$) and two anti-phase ($\phi = \pi$) excitation pulses.

ensemble, will show reduced residual oscillations. In fact in such averaging we find only 10% contrast in wave packet interference, consistent with the expectation from the bulk absorption spectrum. The individual molecules show typically 20 to 60% contrast. Moreover the wave-packet oscillations persist over ~100 fs, longer than the 20–50 fs dephasing time expected from the bulk spectrum. Evidently the selection of a single molecule, with a given conformation of its environment, does lift the ensemble phase averaging effects, allowing larger interference contrasts and therefore superior coherent control.

A crucial element in coherent control is of course the sensitivity to the phase of the optical field. So far we have kept the carrier phase difference between the delayed excitation pulses fixed to zero ($\phi = 0$), while purely varying the delay Δt. Now Fig. 4b also shows the effect of phase: for one and the same molecule the pulse delay response was recorded for both carrier phase difference in-phase ($\phi = 0$) and anti-phase ($\phi = \pi$). Clearly the inverse phase response is observed, confirming the actual phase control. Here it should be noted again that the excitation power has been kept constant in all cases. Thus the decreased response at short time delay (Δt) for the anti-phase ($\phi = \pi$) pulses is a molecular response and not the result of self-interference between the pulse pair.

5. Coherent control of single molecules

Clearly for maximum coherent control each molecule will have its optimal condition in (ϕ, t) phase space of the excitation field. Scanning of time delay or flipping phase by π allows to probe coherent excited state dynamics and gives encouraging clues about the controlled preparation of superposition states, however for complete insight one needs to explore the full (ϕ, t) phase space. Implementation of some feedback algorithm might be the obvious suggestion. However, a single molecule only emits 10^5–10^8 photons before the inevitable photo-bleaching. Thus even a "good molecule" providing 10^6 photocounts and up to a minute observation time, provides no room for feedback. To explore phase space we have designed a series of multiple pulses (four) and systematically varied both their mutual delay time and phase difference. The resulting time-phase response for a chosen molecule is plotted in Fig. 5. Indeed the presented single molecule fluorescence in time-phase space does show clear maxima and minima at certain time-phase combinations. A ~ 50% maximum is observed at $\Delta t = 25$ fs with $\phi = 0.5\ \pi$ and a ~ −50% minimum at $\Delta t = 25$ fs with $\phi = 1.5\ \pi$, again confirming the phase control, when switching to

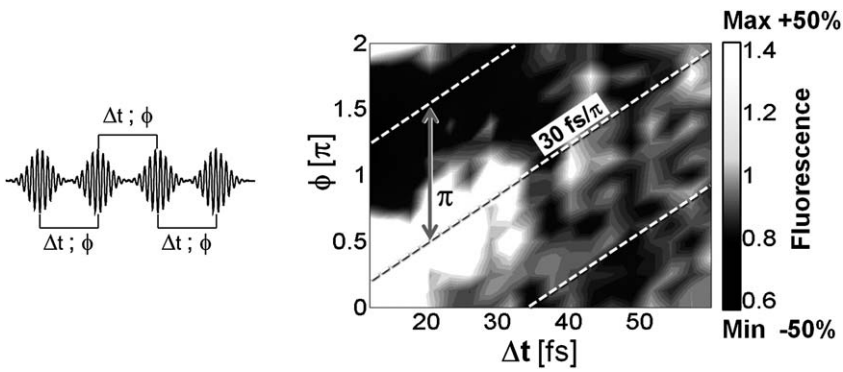

Fig. 5 Coherent control of a single molecule: (left) Excitation by a set of four fs pulses, with controlled time delay (Δt) and carrier envelop phase difference (ϕ) between each consecutive pulse in the sequence; (right) single-molecule time-phase coherent excitation map. The fluorescence intensity is normalized to the average. Dashed lines, separated by π in phase, indicate the progression of maximum and minimum response in phase space.

anti-phase. The ratio between the maximal and minimal response is max/min $\approx$ 3: a fairly high ratio for coherent control experiments, especially at room temperature. The π-shifted maxima and minima follow time-phase lines with a slope of about 30 fs/π for the chosen molecule. The wave-packet phase evolution can be traced by the optical field, providing an indication of the wave-packet group velocity. Moreover tracing the time-phase line one can deduce a decoherence time of about 40 fs.

6. Conclusions

The presented data clearly establishes the feasibility of coherent control of single molecules at room temperature, thus introducing ultrafast spectroscopy into the realm of individual quantum systems. By tailoring the driving fs field to the excitation spectrum of a chosen molecule superior control is achieved and the coherent dynamics of each individual molecule can be traced.

Here it should be noted that the presented results on single molecule coherent control rely on single photon excitation, performed in the weak field limit. Therefore the measured excitation probability as a function of temporal femtosecond pulse delay has a direct equivalence in the spectral domain, linked by the Fourier principle. Concretely, in the limit of infinite measurements, pure amplitude shaping in the linear regime gives the same information as a frequency scan when performed on a closed quantum system. However, even absorption spectroscopy of a single molecule at room temperature has not been shown yet, as it is very challenging due to the photo-dissociation problem.

More importantly, the DN-QDI molecules are embedded in a PMMA polymer matrix, and the interaction with the polymer host is the main source of the observed heterogeneity. As such the molecule-polymer system represents an open (not-closed) quantum system, for which the linear relation between temporal and spectral linear spectroscopy breaks down.[35] Thus the presented use of shaped femtosecond pulses allows preparing superposition states that cannot be achieved by pure CW excitation, and direct monitoring of the ultrafast dynamics of these states, providing insight beyond linear spectroscopy. As an example we recently presented the observation of Rabi oscillations and optical free-induction decays (OFID) of individual molecules.[36] Ultimately the use of fs pulses opens the way to coherent control of multiphoton excitations, which have no linear spectral equivalent in either open or closed systems.

The presented single molecule sensitivity extends the potential of coherent control into the direction of even more complex systems and environments. Particularly the issue of long-lived coherences in pigment-protein complexes is an obvious case that will benefit on the study of individual complexes. Similarly quantum coherences in single organic molecules could be exploited, for basic quantum optics operations.[36] Furthermore coherences in the excited state dynamics of large conjugated polymeric complexes will be of interest. Also, multi-parameter correlations, such as the relation between molecular conformation and function, can be obtained through single-molecule detection. On another note, the fs dynamics in individual plasmonic nanoparticles, nano-antennas or emitter-antenna systems could be controlled.

Despite these interesting prospects one has to be realistic as to practical implications. Firstly, the presented work is based on terrylene derivatives, which are extremely efficient and photostable chromophores, with close-to-unity quantum efficiency and photo-bleaching rate of only 10^{-8}–10^{-7} per optical cycle, *i.e.* ideal for single molecule detection. More common dyes or protein complexes are typically $\sim$100 times less photostable, making ultrafast studies a real challenge. Secondly, it is crucial that the broad band fs pulse is Fourier limited with flat spectral phase in the focus of the confocal microscope. High NA oil immersion objectives introduce extensive dispersion which requires major compensation. Finally, one relies on the detection fluorescence intensity of a molecule: any change in the excitation conditions, spatial or temporal, will affect the recorded signal and can lead to artefacts.

Particularly the spatial shaping, which is concomitant to any phase shaper (spectral or temporal), can cause spatio-temporal coupling, which should be avoided.[34]

Currently we are exploring the ultrafast intra-complex dynamics of electronic excitations in individual light-harvesting (LH2) complexes of purple bacteria.

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