

Supplementary Information: Visualising Hidden Ultrafast Processes in Individual Molecules by Single-Pulse Coherent Control

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Experimental measurements

Ensemble spectroscopy on MeLPPP

Figure 2 in main text shows the linear (one-photon) absorption spectrum of a solution of MeLPPP in toluene (black solid line, main panel). The absorption maximum occurs around 22000 cm^{-1} , which corresponds to the transition from the ground vibrational level of the electronic ground state S_0 to the ground vibrational level of the first electronic excite singlet state S_1 . The green line represents the PL spectrum, which stems from the (one-photon) transition $S_1 \rightarrow S_0$. Both (one-photon) spectra are accompanied by a well-resolved vibronic progression, reflecting the coupling of the electronic transition mainly to carbon-bond stretch vibrations with energies of $\sim 1500\text{ cm}^{-1}$.

The inset in Fig. 2 in the main text displays the PL-detected two-photon excitation spectrum for the transition from the ground vibrational level of S_0 to the second electronically excited singlet state S_2 (data taken from Ref.¹). Upon excitation of state S_2 , rapid population relaxation within $\sim 150\text{ fs}$ into the photoluminescent state S_1 occurs,² i.e., the PL intensity reports on the relative probability of population transfer into the two-photon accessible state S_2 as described in the main text. The two-photon spectrum shows its maximum around 26380 cm^{-1} , corresponding to the purely electronic two-photon transition. The peak at a still higher energy of 27670 cm^{-1} reflects the transition into a vibrational state (carbon-bond stretch) of S_2 .

In our single molecule experiments, we used a laser spectrum centred around 13000 cm^{-1} with a full width at half maximum of $\sim 400\text{ cm}^{-1}$, see Fig. 2 main text. Thus the first excited state S_1 is far from one-photon resonance. Although two-photon excitation into high vibrational levels of S_1 are in principle possible, we demonstrated previously that the rigid-rod-like structure of MeLPPP enforces strict symmetry selection rules for optical transitions.¹ For MeLPPP the wave functions of the electronic states possess alternating even and odd parity with increasing energy. Hence, two-photon transitions from the even parity ground state S_0 into the odd parity lowest-energy excited state S_1 are essentially forbidden. In contrast, two-photon transitions into the even parity state S_2 are strongly allowed (and can even be induced by continuous-wave excitation).

In our simulations, we fixed the energy of the state S_1 at $E_1 = 22000 \text{ cm}^{-1}$, and we ignored optical transitions to S_1 , which can only be populated by population relaxation (internal conversion) from S_2 . The vibrational peak in the two-photon spectrum is offset by around 1300 cm^{-1} from the electronic transition into S_2 . Given the limited bandwidth of the laser pulse used, this implies that we are only resonant with the electronic $S_0 \rightarrow S_2$ transition. Thus vibrational levels in S_2 can be safely excluded in our model.

Optical free induction decay of single MeLPPP molecules

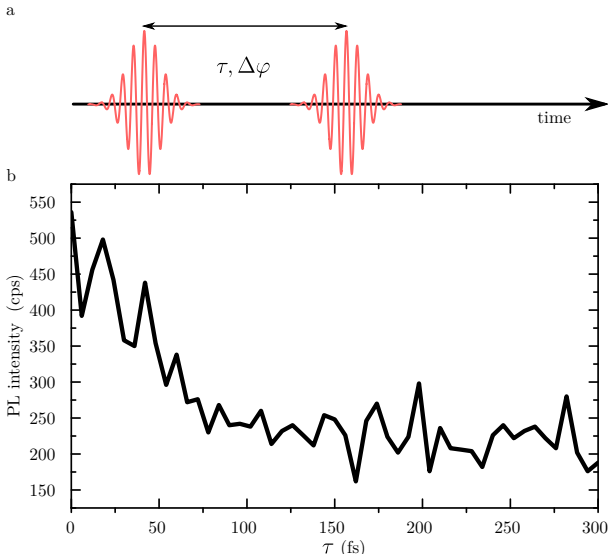


Figure S1: **Two-photon induced optical free induction decay envelope of a single MeLPPP molecule.** **a:** A sequence of phase-locked ($\Delta\varphi = \text{constant}$) femtosecond laser pulses with time delay τ is used to drive the two-photon $S_0 \rightarrow S_2$ transition. **b:** Example of the PL signal as a function of delay time for a single MeLPPP molecule at room temperature.

To determine the electronic dephasing rate γ_2 of state S_2 directly, we measured the envelope of the optical free induction decay (oFID) on single MeLPPP molecules upon two-photon excitation. A pair of identical time-delayed and phase-locked femtosecond laser pulses with a centre frequency of $\sim 13000 \text{ cm}^{-1}$ and a bandwidth of $\sim 400 \text{ cm}^{-1}$ is created by amplitude shaping (Fig. S1a). The general idea behind this approach³ is that the first pulse in such a sequence creates a coherent superposition between S_0 and S_2 wave functions by a two-photon process. The phase

memory between these wave functions, however, is rapidly destroyed by interaction with a complex, temporally fluctuating environment at room temperature. The second time-delayed pulse with fixed phase relation relative to the first pulse then probes the decay of this coherent superposition. This coherence decay is reflected in a reduced ability to transfer population to the second excited state by the time-delayed pulse, which results in a reduced PL signal with increasing delay time.³ Figure S1b shows a PL trace as a function of the delay time τ (with constant inter-pulse phase difference) for a single MeLPPP molecule. From this oFID, a dephasing rate of the order of $1/50 \text{ fs}^{-1}$ can be retrieved, consistent with the simulated rates given in the main text and the tables S1 and S2 below. However, measuring both, the oFID and β dependent traces, shown in the main text, is extremely difficult due to the still limited photostability of the molecules at the relatively high excitation powers used here. Therefore, the oFID-measurement is only used to verify the correct order of magnitude for the dephasing rates taken for the simulations.

In this context, we note that low-energy ($< 100 \text{ cm}^{-1}$) matrix vibrational modes couple to the purely electronic transitions in MeLPPP. These modes give rise to broad, featureless shoulders in the low-energy tail of the purely electronic transitions in static low-temperature (1.5 K) single-molecule spectra.⁴ The pronounced temperature dependence of the electron-phonon coupling strength to such low-energy modes,⁵ however, results in a strong line broadening and increase in relative intensity of these modes. At room temperature only a single broad line is therefore observed for the electronic transition in optical spectra, which can be treated as a single, effective transition.³ In other words, at room temperature the coupling to matrix modes provides the decohering environment, which is captured in our theoretical simulations by the dephasing rates.

Theoretical analysis and simulations

Non resonant two-photon transition probability

We consider first an isolated two-level quantum system without interaction with its environment. The wave functions of the two levels are $|g\rangle$ and $|f\rangle$ with energies E_g and E_f , respectively. For

a non-resonant two-photon excitation from the ground state $|g\rangle$ to the final state $|f\rangle$ induced by a time-dependent laser field $\mathcal{E}(t)$, the time-dependent amplitude $a_f(t)$ of state $|f\rangle$ at time t can be derived from second-order perturbation theory

$$a_f(t) = -\frac{1}{\hbar^2} \sum_{\nu} \mu_{f\nu} \mu_{\nu g} \int_{-\infty}^t \int_{-\infty}^{t_1} \mathcal{E}(t_1) \mathcal{E}(t_2) e^{i\omega_{f\nu}t_1} e^{i\omega_{\nu g}t_2} dt_2 dt_1. \quad (\text{S1})$$

Here $\mu_{f\nu}$ and $\mu_{\nu g}$ are the one-photon transition dipole moments, $|\nu\rangle$ is a manifold of virtual states, $\omega_{f\nu} = (E_f - E_{\nu})/\hbar$, and $\omega_{\nu g} = (E_{\nu} - E_g)/\hbar$. The probability of non-resonant two-photon transition from $|g\rangle$ to $|f\rangle$ is then given by

$$\begin{aligned} P_{g \rightarrow f} &= \left| -\frac{1}{i\hbar^2} \sum_{\nu} \frac{\mu_{f\nu} \mu_{\nu g}}{\omega_{\nu g} - \omega_{fg}/2} \int_{-\infty}^{\infty} E(\omega) E(\omega_{fg} - \omega) d\omega \right|^2 \\ &= \left| -\frac{D_{gf}^2}{i\hbar^2} \int_{-\infty}^{\infty} A(\omega) A(\omega_{fg} - \omega) e^{i\phi(\omega) + i\phi(\omega_{fg} - \omega)} d\omega \right|^2 \end{aligned} \quad (\text{S2})$$

where D_{gf} denotes effective two-photon transition dipole moment between states $|g\rangle$ and $|f\rangle$, $A(\omega)$ is the laser spectral amplitude that is unchanged in our experiments. Since a quadratic spectral phase $\phi(\omega) = \beta(\omega - \omega_0)^2/2$ is used, the maximal probability $P_{g \rightarrow f}$ occurs at $\beta = 0$, i.e., using the transform-limited pulse. Furthermore, the probability $P_{g \rightarrow f}$ decreases by increasing the absolute value of β , and therefore exhibits a symmetric distribution with respect to chirp rate β . If the quantum system is embedded in a disordered environment, the response of $P_{g \rightarrow f}$ to chirp rate β will be scaled, whereas it remains symmetric. As a result, the asymmetric traces observed in our experiments imply that the underlying photoexcitation process goes beyond the pure non-resonant two-photon excitation model.

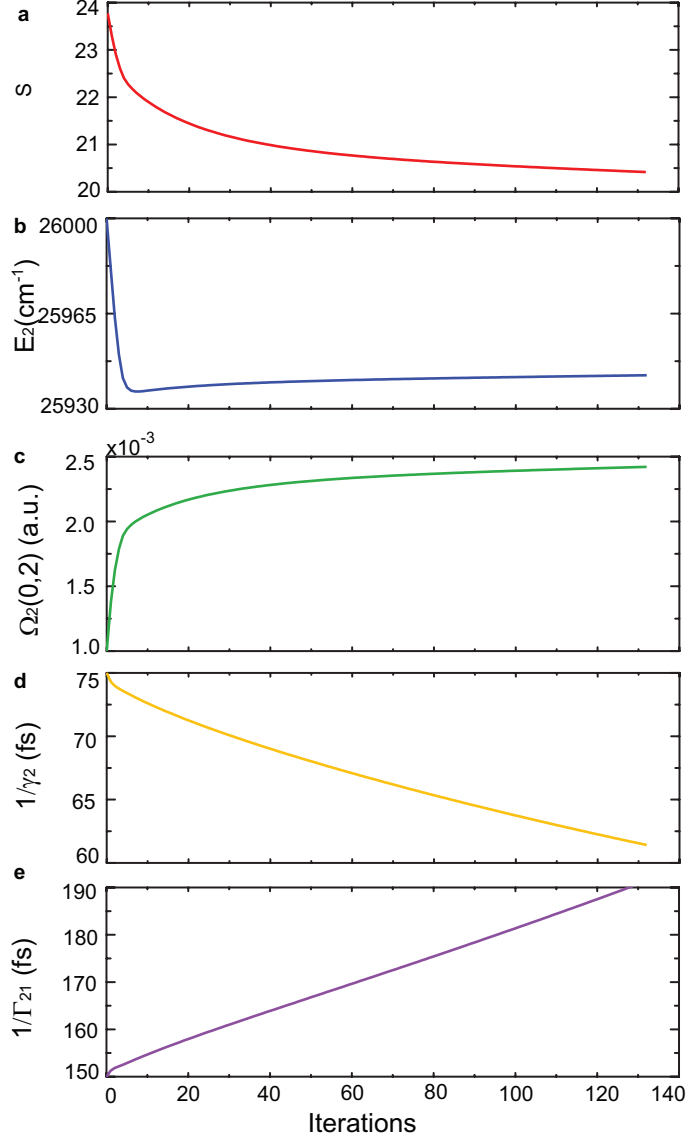


Figure S2: **Quantum Dynamics Identification of two-photon excitation within a three-level model.** **a:** Residual (estimator) s , **b:** the energy E_2 of the two-photon accessible level S_2 , **c:** the two-photon Rabi frequency $\Omega_{2P}(0, 2)$, **d:** the dephasing time $1/\gamma_2$ of level S_2 , and **e:** the relaxation time $1/\Gamma_{21}$ as a function of iterations. Here we show the parameter estimation for the specific molecule in Fig. 3 of the main text.

Quantum Dynamics Identification

To evaluate the quality of the Quantum Dynamics Identification, we define a residual estimator at each iteration by

$$s = \sqrt{\sum_{m=1}^M \frac{\mathcal{P}_m(\beta_m) - [aP_m(Q, \beta_m) + b]}{M-2}} \quad (\text{S3})$$

where $\mathcal{P}_m(\beta_m)$ and $P_m(Q, \beta_m)$ are experimentally measured PL signals and theoretically calculated quantum yields, respectively, and the corresponding parameters a and b are adaptively updated. Fig. S2 shows the parameter optimization for the example of the molecule shown in Fig. 3 of main text based on the minimal three-level model with four free parameters, i.e., the energy E_2 of state S_2 , the two-photon Rabi frequency $\Omega_{2P}(0, 2)$, the dephasing rate γ_2 and relaxation rate Γ_{21} of level S_2 . The gradient-based optimization algorithm as indicated in main text leads to a monotonic convergence of the residual, and the “optimal” parameters are found, which are clearly different from the initial guess. Note that the rate of convergence and the value of s are dependent on the initial guess, which only may lead to local minima of s in the parameter space (not necessarily to the global minimum). As a result, the identified model may not be unique, especially in the presence of noises. In our procedure, we performed a number of simulations with different initial guesses, and we restricted us to find a minimal model with physically reasonable parameters. Importantly, we did not see any significant improvement of s for different initial guesses of the parameters. The estimated values of parameters are in line with the known values or consistent with complementary measurements, although we did not involve any constraints on estimating such parameters. However, we would like point out here that the uniqueness of the identified model is a fundamentally important problem in quantum system identification. Prior knowledge from ensemble (e.g., absorption/emission spectrum) is very helpful to either speeding up the convergence or determining a physically reasonable model.

Time-dependent population dynamics within the three-level model

Based on the identified three-level model for the specific molecule shown in Fig. 3 of the main text, with the optimal parameters in Fig. S2, we can reconstruct the time-dependent excited state population dynamics for this molecule, see Fig. S3, to characterise both coherent and dissipative processes. The two-photon transition takes place between the states S_0 and S_2 , from which the population rapidly decays to the first electronic excited state S_1 .

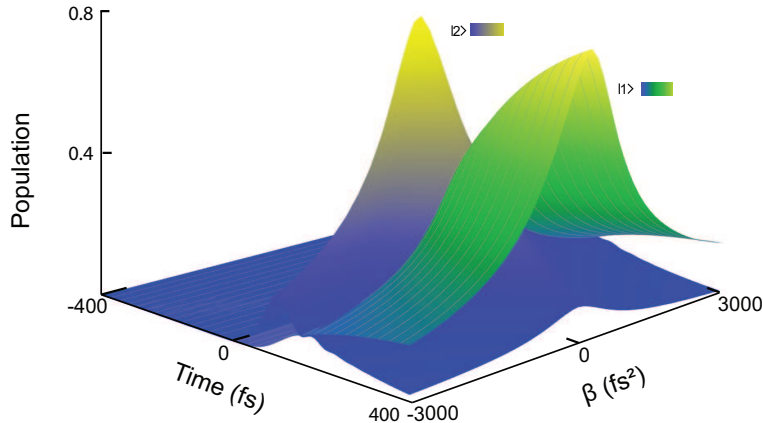


Figure S3: **Reconstruction of time-dependent population dynamics.** The population dynamics in the electronic states S_1 and S_2 were calculated within the three-level model with the same parameters as used for Fig. 3 in the main text.

Three-level model simulations

Figure S4 shows the three-level model simulations for two additional single molecules with symmetrical behaviour as in Fig. 3 of the main text.

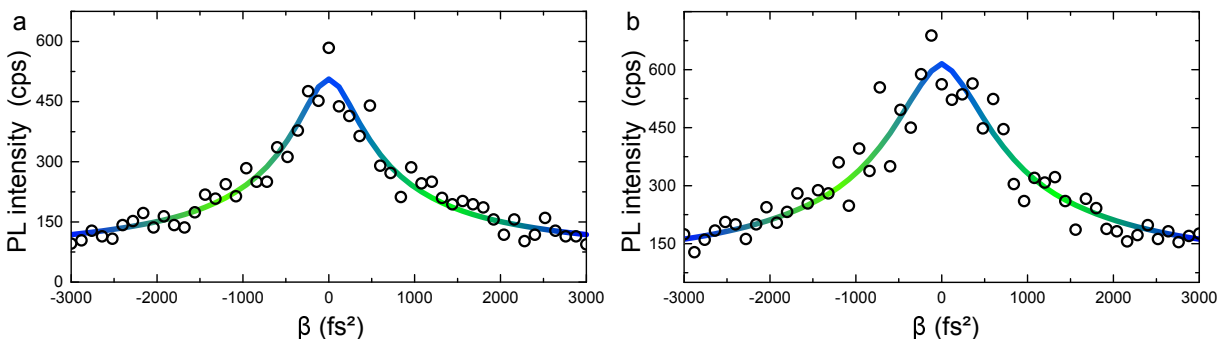


Figure S4: **Three-level model simulations.** Chirp-dependent PL signals of two different single MeLPPP molecules (circles) and theoretical simulations (colored solid line). The estimated values of the free parameters are listed in Table S1.

Interestingly, for all molecules investigated here the energies E_2 of state S_2 are red-shifted by up to 500 cm^{-1} with respect to the corresponding energy determined from the ensemble spectrum (Fig.2 in main text). As mentioned in the main text, this red-shift substantially improves spectral overlap between the laser and the two-photon transition for the single molecules. Hence, a higher PL is observed from these molecules as compared to a molecule with an energy E_2 similar to the ensemble value. This systematic red-shift is thus consistent with the fact that in single-molecule

Table S1: Three-level simulation parameters for molecules with symmetric PL response.

	Energy(cm^{-1})	Rabi frequency(cm^{-1})	Decay rate(fs^{-1})	
	E_2	Ω_{2P}	γ_2	Γ_{21}
Molecule Fig.3	25940	531	1/61	1/191
Molecule Fig.S4(a)	26039	198	1/65	1/179
Molecule Fig.S4(b)	25923	590	1/83	1/135

experiments usually the brightest molecules are pre-selected.

Moreover, the dephasing rates γ_2 and the relaxation rates Γ_{21} (for the internal conversion from S_2 to S_1) are all in the range expected from our oFID measurements and literature data.²

Four-level model simulations

Table S2 lists the optimal values of the seven free parameters used for the simulation of the molecules with an asymmetric chirp-dependent PL response shown in Fig. 4 in the main text.

Table S2: Four-level simulation parameters for molecules with asymmetric PL response.

	Energy(cm^{-1})		Rabi frequency(cm^{-1})		Decay rate(fs^{-1})		
	E_2	E_3	Ω_{2P}	Ω_{1P}	γ_2	γ_3	Γ_{21}
Molecule Fig.4a	25855	38626	674	366	1/72	1/73	1/152
Molecule Fig.4b	25914	39051	595	151	1/88	1/94	1/140
Molecule Fig.4c	25712	38712	619	338	1/62	1/52	1/172

Time-dependent population dynamics within the four-level model

Figure S5 shows the time-dependent population dynamics for a given chirp, to demonstrate how chirp influences population transfer into the high-lying excited state S_3 and how this determines the shape of the asymmetric PL traces as function of chirp (Fig. 4 of the main text). Figure S5a (left) shows the time-dependent population of the involved states at $\beta = -1560 \text{ fs}^2$ for the molecule in Fig. 4a of the main text. The first obvious observation is that owing to the time-dependent instantaneous frequency ω_i of the chirped pulse the resonance condition for two-photon transition

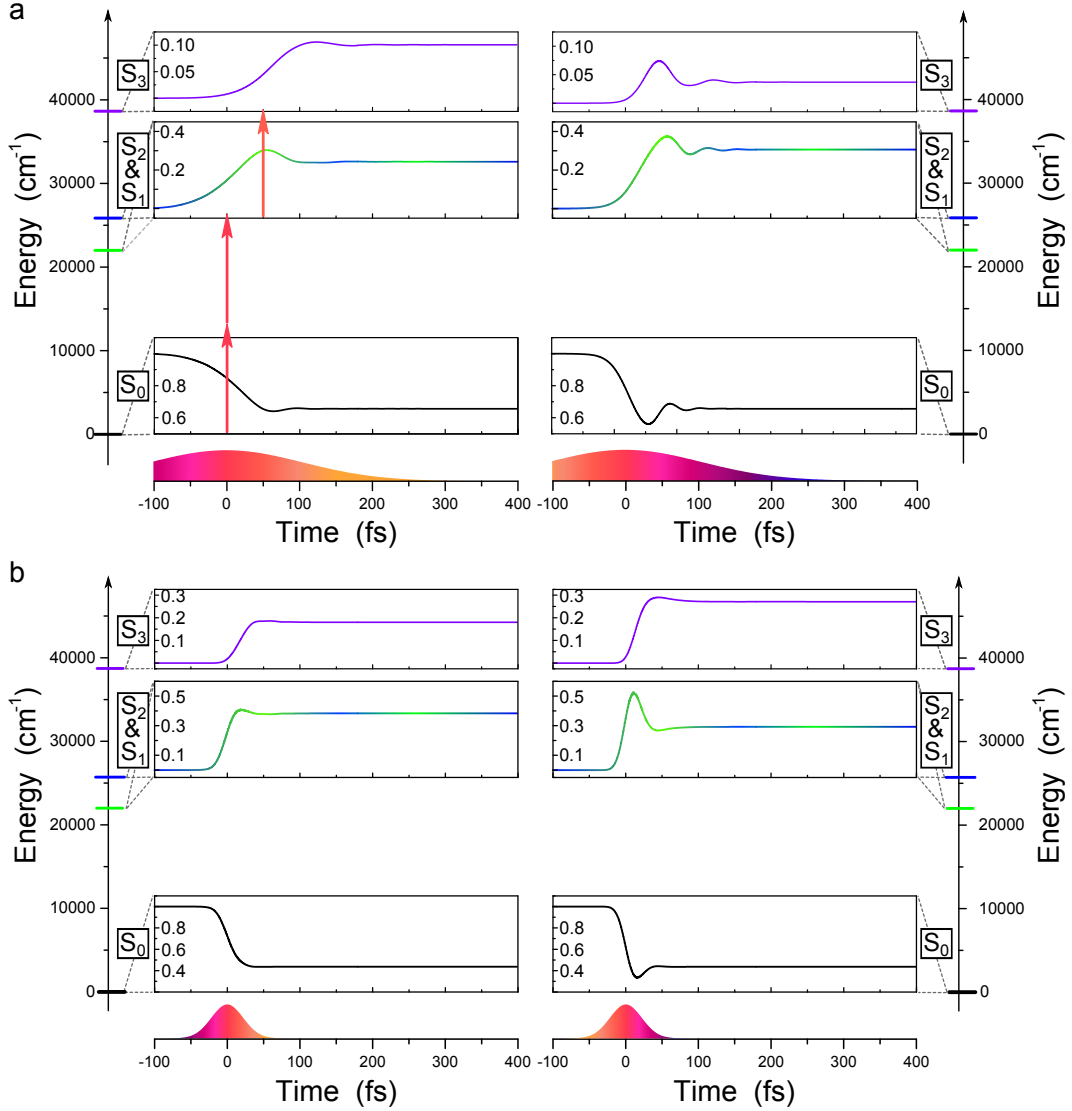


Figure S5: **Time-dependent population dynamics within the four-level model.** **a:** Time-dependent population dynamics of all involved states for the single molecule in Fig. 4a at chirps of $\beta = -1560 \text{ fs}^2$ (left) and 1560 fs^2 (right). **b:** Time-dependent population dynamics of all involved states for the single molecule in Fig. 4c at chirps of $\beta = -240 \text{ fs}^2$ (left) and 240 fs^2 (right).

into state S_2 , i.e. $E_2 = 2 \cdot \hbar\omega_i$, is fulfilled only around 0 fs on the time axis (see rise in S_1 & S_2 and decrease in S_0 in Fig. S5 at red arrows). Yet, at this point in time this instantaneous frequency of the pulse does not allow to access state S_3 via a quasi-instantaneous three-photon process, because for this specific instantaneous laser frequency state S_3 is out of resonance with respect to state S_2 . Only some 10 fs after the two-photon process ω_i fulfills the one-photon resonance condition so that a one-photon transition from S_2 into state S_3 becomes possible. Since S_3 is depopulated

non-radiatively into the ground state, this larger population in S_3 reflects loss for PL, i.e., a reduced PL signal (see asymmetric traces, Fig.3 main text).

For an oppositely chirped pulse ($\beta = +1560 \text{ fs}^2$, see Fig. S5, right) the two-photon transition also takes place around 0 fs. However, the continuously increasing instantaneous laser frequency as function of time gives rise to a suppression of the final one-photon step $S_2 \rightarrow S_3$, because the instantaneous frequency is not large enough anymore ($E_3 - E_2 > \hbar\omega_i$). This is reflected in a substantially smaller population in state S_3 for positive β , or in other words, in a larger PL signal as compared to the corresponding pulse with negative β .

Similar conclusions, though with exactly opposite chirp-dependent behaviour, can be drawn for the example in Fig. S5b, which shows the time-dependent behaviour for $\beta = \pm 240 \text{ fs}^2$ for the molecule in Fig. 4c of the main text. Hence, these time-dependent data clearly demonstrate how the interplay between the specific energy landscape of each molecule, the one-photon Rabi-frequency coupling states S_2 and S_3 as well as the instantaneous frequency of the chirped pulse impacts on the probability for (2+1)-photon interactions and thus on the overall shape of the chirp-dependent PL traces.

Chirp-dependent ensemble measurement

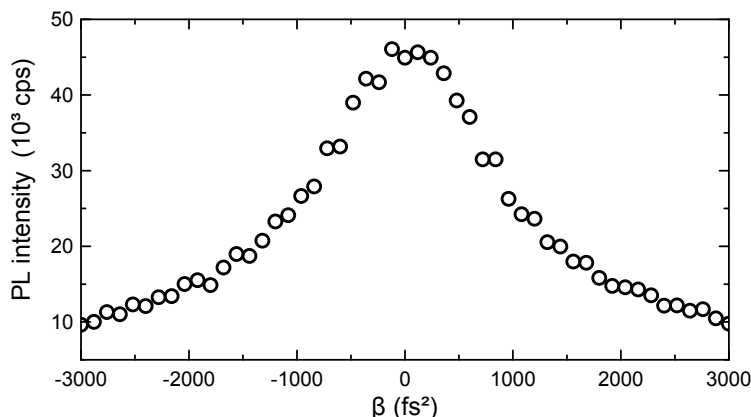


Figure S6: Coherent control experiment on a bulk MeLPPP film at room temperature.

The data in Fig. S6 display the chirp-dependent PL signal for a MeLPPP film measured un-

der the same conditions used for the single-molecule experiments. The ensemble signal is perfectly symmetric and can – in principle – be reproduced by pure two-photon processes between two electronic states, see Eq. (S2). Ignoring the information from our single-molecule data, it might therefore be concluded that in an ensemble only two-photon processes take place. However, the observation of symmetric (two-photon transitions) as well as asymmetric PL traces ((2+1)-photon transitions) in single-molecule experiments rather indicate that in ensemble measurements the asymmetry is averaged out. These data clearly demonstrates the valuable information that can be revealed from single-molecule experiments beyond the ensemble average.

Three-level simulations for asymmetric data

To test whether the asymmetric data sets, shown in Fig. 4 of the main text, can be reproduced with a simpler model, we performed three-level model simulations on these data, see Fig. S7. Although the model could reproduce the data within the given error of the measurement, clear systematic deviations between data and simulations can be seen without any further knowledge. This in turn proves, that the physics behind the asymmetric data sets go beyond a simple two-photon transition between two electronic levels and a more complex model is essential.

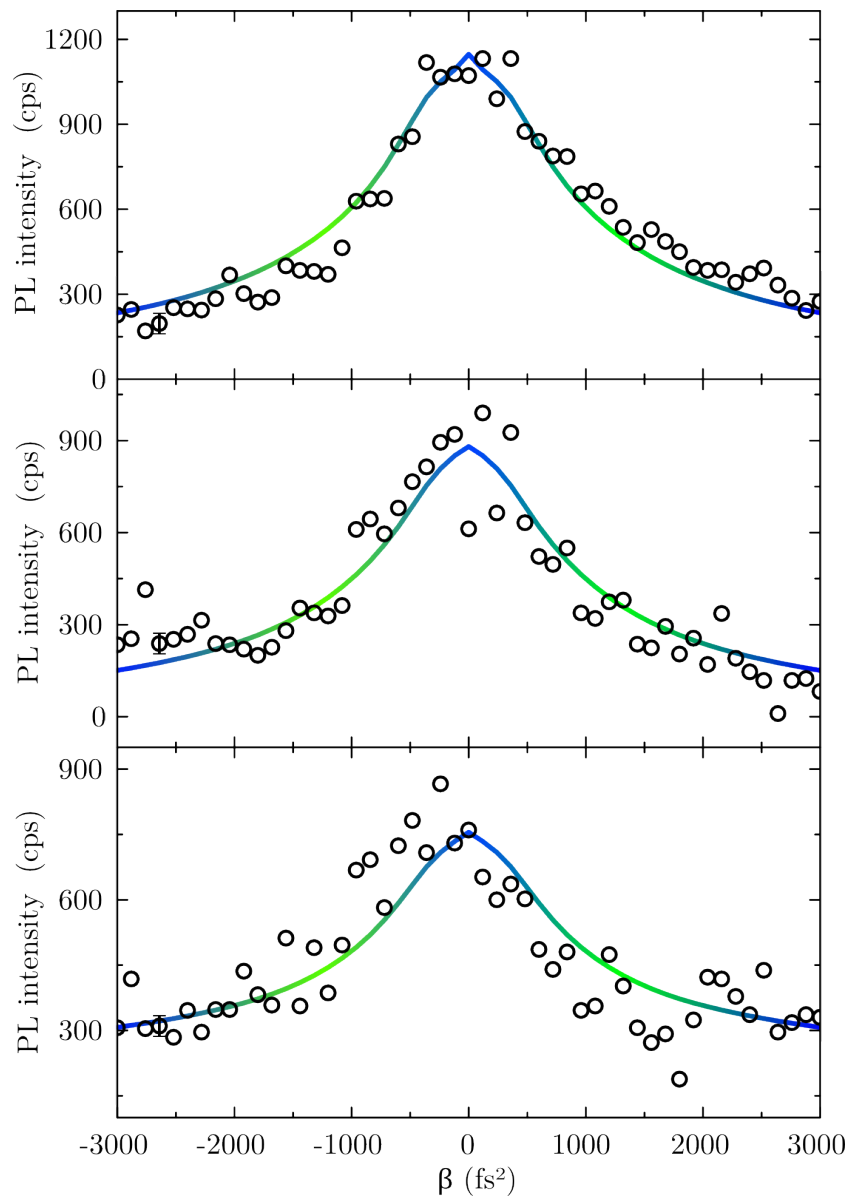


Figure S7: **Three-level model simulations and asymmetric data.** The asymmetric data from Fig. 4 of the main text (open circles) are superimposed with (symmetric) simulations of two-photon transitions between the two electronic levels S_0 and S_2 (solid lines) in single MeLPPP molecules.

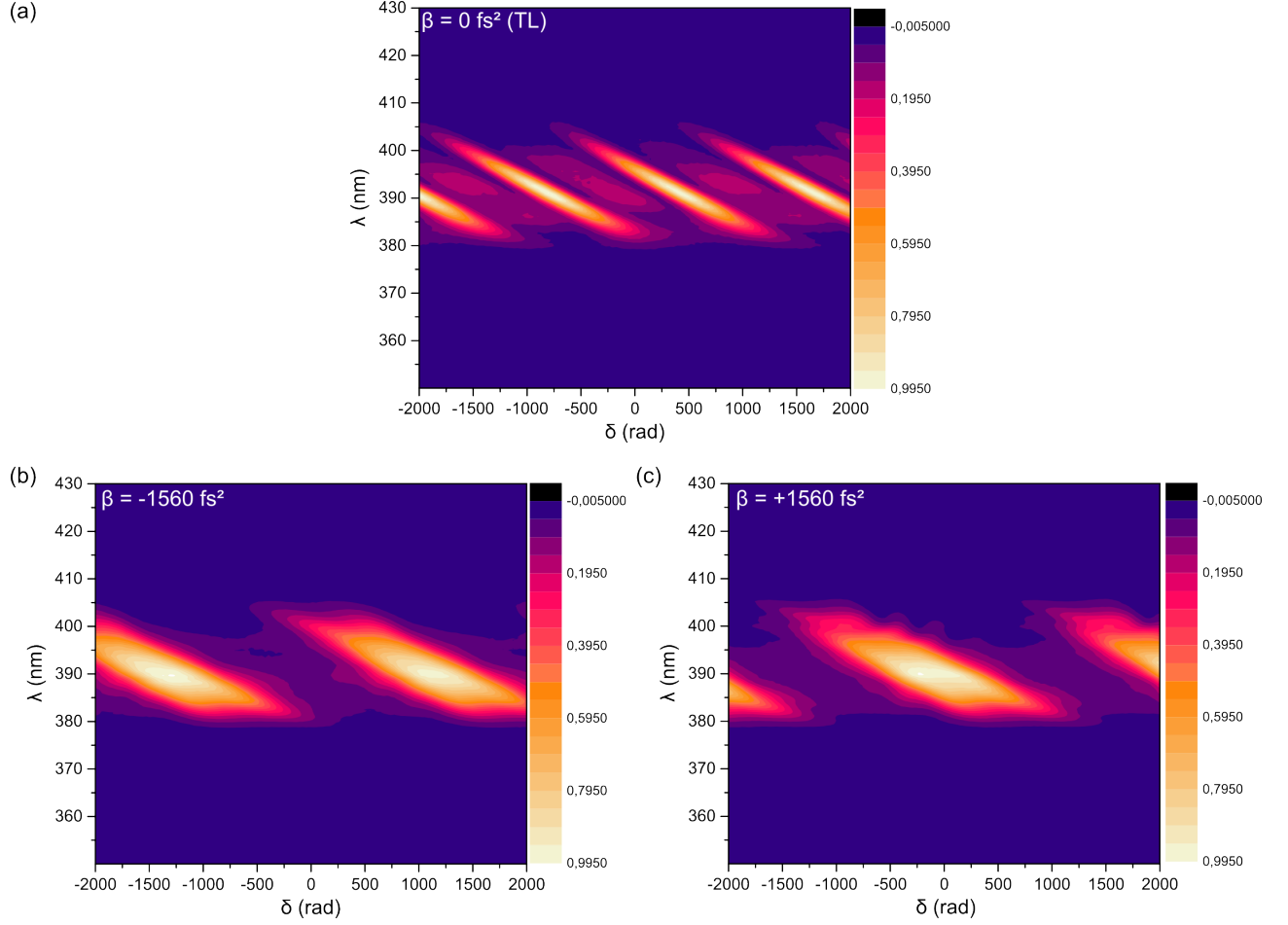


Figure S8: Multi-photon intra-pulse interference phase scan of a transform limited (a) and of linearly chirped pulses with $\beta = \pm 1560 \text{ fs}^2$ (b).

Characterisation of the laser pulse

In order to characterise the spectral chirp we present in Fig. S8 three multi-photon intra-pulse interference phase scans (MIIPS)⁶ of laser pulses for the case of a fully compressed transform limited pulse and exemplarily for two chirped pulses with $\beta = \pm 1560 \text{ fs}^2$. We applied the following phase function⁶

$$\phi(\omega) = 1 \cdot \cos(35\text{fs} \cdot (\omega - \omega_0) + \delta), \quad (\text{S4})$$

where δ was scanned from -2000 to 2000 rad and ω_0 was set to the maximum of the laser spectrum at 13000 cm^{-1} . These MIIPS data clearly show the expected behaviour for transform limited and positively (negatively) chirped pulses.

Single Molecule Measurement Character

In order to proof the single emitter character of our sample we recorded the two-photon induced PL as a function of time for two different MeLPPP molecules (see Fig.S9). The red dashed lines are guides to the eye, which illustrate the “digital” switching of the PL signal between to distinct (“on” and “off”) levels (blinking events at $\sim 35s$ for the molecule in (a) and at $\sim 13s, 28s$ for the molecule shown in (b)). Since the lower red line is at the background level of our measurements (100 - 200 counts per second), the observed digital blinking character clearly demonstrates single molecule behaviour.

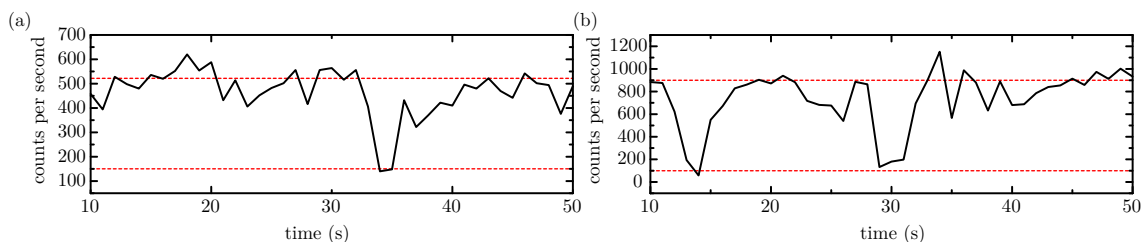


Figure S9: **Single-Molecule Blinking Traces.** Two-photon induced photoluminescence detected as function of time for two different molecules. The red dashed lines are guides to the eye line and indicate the two levels between which the molecules are switching.

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