SUPPORTING INFORMATION

Photon Correlation Spectroscopy of Luminescent Quantum Defects in Carbon Nanotubes

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I. Cryogenic photoluminescence of nanotubes with strong and weak cross-correlations

Supplementary to the cryogenic spectra shown in Fig. 1b of the main text, Fig. S1 shows a set of photoluminescence (PL) spectra of individual hot-spots of our sample with hexyl-functionalized (6,5) single-walled carbon nanotubes (CNTs). The blue, green and red shaded areas indicate the spectral bands of emission from $E_{11}$, X and T, respectively. Note that the PL intensities within different spectral bands were not corrected for the spectral variation in the quantum efficiency of the InGaAs detector used to record PL.

We first focus on the left column of Fig. S1 with PL spectra of CNTs with strong cross-correlations. Fig. S1b and c show the most simple case of one peak within each spectral band of $E_{11}$, X and T, whereas the spectrum of CNT A of the main text, shown in Fig. S1b, features a double-peak feature in the spectral band of X. In auto-correlation, the latter exhibits strong antibunching as a hallmark of single-photon single-defect emission. Thus, the double-peak feature is consistent with temporally switching configurations of a single-defect in agreement with previous reports for cryogenic nanotubes with exciton-localizing unintentional defects1 and defect-functionalized CNTs.2 Strong cross-correlations within X and T bands support this interpretation.

![Figure S1](image_url)

Figure S1. (a)-(c) Cryogenic spectra of three CNTs with strong cross-correlations. The spectrum in (a) corresponds to the CNT A of the main text. (d)-(f) Cryogenic spectra of three CNTs with weak cross-correlations. The spectrum in (d) corresponds to the CNT B of the main text. The spectral regions of $E_{11}$, X and T emission are shaded in blue, green and red, respectively.
In the right column of Fig. S1 we show PL spectra for CNTs with weak cross-correlations, and Fig. S1d shows the spectrum of CNT B discussed in the main text. In support of our interpretation, the spectrum features pairs of peaks within both X and T spectral bands fully consistent with PL from two spectrally dissimilar defects. The spectrum of Fig. S1e is similar albeit with a very weak second peak in the T band. The spectrum in Fig. S1f, on the other hand, contrasts this consistency by exhibiting a single-peak features within X and T spectral bands. As the scenario of two proximal defects with spectrally identical emission seems rather unrealistic, consistency can be established if we assume that the second defect was switched off during the acquisition of the spectrum yet switched on during photon correlation spectroscopy measurements. This exotic case, as well as the cases of CNTs with strong cross-correlations, were chosen to highlight explicitly the rich variety of observations in time-averaged and photon correlation spectroscopy, including rare cases that elude self-consistent interpretation.

II. Blinking single-photon source with one emissive state

To model the PL of CNTs with signatures of intermittent single photon emission, we employ the three-level system in Fig. S2 comprising the ground state |0⟩, a bright state |B⟩ and a dark state |D⟩. While the dynamics of this system can be readily formulated in terms of the rate equation

$$\frac{d}{dt} \begin{pmatrix} p(0)(t) \\ p(B)(t) \\ p(D)(t) \end{pmatrix} = \begin{pmatrix} -\gamma_{\text{abs}} & \gamma_{\text{rad}} & 0 \\ \gamma_{\text{abs}} & -\gamma_{\text{rad}} - \kappa_s & \kappa_d \\ 0 & \kappa_s & -\kappa_d \end{pmatrix} \begin{pmatrix} p(0)(t) \\ p(B)(t) \\ p(D)(t) \end{pmatrix},$$

(S1)
a general analytic solution leads to lengthy expressions that impede an intuitive interpretation. For many realistic scenarios, however, additional assumptions can be used to simplify the theoretical description. Typically, the dynamics between the bright state |B⟩ and the dark state |D⟩ is slower than both excitation and relaxation, such that $\gamma_{\text{abs}}, \gamma_{\text{rad}} \gg \kappa_s, \kappa_d$. In this case, higher order terms of the form $\kappa/\gamma$ can be omitted, where $\kappa$ stands for either $\kappa_s$ or $\kappa_d$ and $\gamma$ stands for either $\gamma_{\text{abs}}$ and $\gamma_{\text{rad}}$.

Based on this simplification, we will derive a product form for the second order correlation function $g^{(2)}$, Eq. (S9), where the two factors describe the contributions of PL intermittence (blinking) and single-photon emission, respectively. In particular, we find that single-photon emission is solely determined by the dynamics within the two-level sub-system comprising the states |0⟩ and |B⟩, while the blinking behavior originates from the two-level sub-system comprising the states |B⟩ and |D⟩.

For brevity we skip the lengthy derivation of a general solution to Eq. (S1) and directly proceed to find the two contributions from both two-level sub-systems in Fig. S2. This ansatz implicitly assumes a perfect decoupling of the dynamics in both two-level sub-systems that is only accurate in the case $\gamma_{\text{abs}} \gg \gamma_{\text{rad}}$. Corrections that arise when $\gamma_{\text{abs}} \gg \gamma_{\text{rad}}$ does not hold, will be discussed after the derivation of Eq. (S9).

For both two-level sub-systems we use rate models to find analytic expressions for the second order correlation function given by

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} = \frac{\langle I_0p(t) \cdot I_0p(t+\tau) \rangle}{\langle I_0p(t) \rangle^2} = \frac{\langle p(t)p(t+\tau) \rangle}{\langle p(t) \rangle^2},$$

(S2)

where $\langle \cdot \rangle$ is the average over time $t$, $I(t)$ is the measured intensity at time $t$; $I_0$ is the time-averaged emission intensity and $p(t)$ is the probability to detect a photon at time $t$.

We first focus on the two-level sub-system comprising the states |B⟩ and |D⟩ (left part in Fig. S2) that describes shelving from a bright state |B⟩ into a dark state |D⟩ with rate $\kappa_s$ and deshelving with rate $\kappa_d$. The dynamics of this two-level system is

![Figure S2. Three-level system comprising the ground state |0⟩, a bright state |B⟩ and a dark state |D⟩ with corresponding transition rates. The two-level sub-systems comprising the states |0⟩ and |B⟩ and comprising the states |B⟩ and |D⟩ are used to model photon antibunching due to single-photon emission and bunching arising from PL intermittence (blinking), respectively.](image_url)
To formulate a model that captures both bunching due to PL intermittence and antibunching due to single-photon emission, we formulate by the rate equation

\[
\frac{d}{dt} \left( \frac{p_{[B]}(t)}{p_{[D]}(t)} \right) = \begin{pmatrix} -\kappa_s & \kappa_d \\ \kappa_s & -\kappa_d \end{pmatrix} \left( \frac{p_{[B]}(t)}{p_{[D]}(t)} \right),
\]

where \( p_{[\psi]}(t) \) is the probability to find the system in state \(|\psi\rangle\) at time \( t \). In the steady state limit, both \( \langle p(t) \rangle \) and \( \langle p(t + \tau) \rangle \) in Eq. (S2) are given by the time-independent probability \( p_{[B]}(\infty) \) to find the system in the bright state \(|B\rangle\), since there is no photon emission from the dark state \(|D\rangle\). For the numerator in Eq. (S2) we find

\[
\langle p(t)p(t + \tau) \rangle = \langle p_{[B]}(t) \cdot p_{[B] \rightarrow [B]}(t + \tau|t) \rangle = \langle p_{[B]}(t) \cdot p_{[B] \rightarrow [B]}(\tau) \rangle = p_{[B]}(\infty) \cdot p_{[B] \rightarrow [B]}(\tau),
\]

where \( p_{[B] \rightarrow [B]}(t + \tau|t) \) is the probability to find the system in state \(|B\rangle\) both at time \( t \) and \( t + \tau \), and \( p_{[B] \rightarrow [B]}(\tau) \) is the probability for returning from state \(|B\rangle\) to state \(|B\rangle\) after time difference \( \tau \). By solving Eq. (S3) we find \( p_{[B]}(\infty) = \kappa_d/(\kappa_s + \kappa_d) \) and \( p_{[B] \rightarrow [B]}(\tau) = \kappa_d/\kappa_s + \kappa_d) + \kappa_s/\kappa_s + \kappa_d) \cdot \exp[-(\kappa_s + \kappa_d)|\tau|] \) and with the inverse rates \( \tau_s = 1/\kappa_s \) and \( \tau_d = 1/\kappa_d \) we obtain the result of Santori et al.\(^4\) for blinking self-assembled quantum dots,

\[
g^{(2)}(\tau) = 1 + \frac{\kappa_s}{\kappa_d} e^{-(\kappa_s + \kappa_d)|\tau|} = 1 + \frac{\tau_d}{\tau_s} e^{-\left(\frac{\tau_s}{\tau_d} + \frac{\tau_d}{\tau_s}\right)|\tau|}.
\]

For the case of single photon emission we consider the two-level sub-system comprising the states \(|0\rangle\) and \(|B\rangle\) (top part in Fig. S2) that can be described by the rate equation

\[
\frac{d}{dt} \left( \frac{p_{[0]}(t)}{p_{[B]}(t)} \right) = \begin{pmatrix} -\gamma_{abs} & \gamma_{rad} \\ \gamma_{abs} & -\gamma_{rad} \end{pmatrix} \left( \frac{p_{[0]}(t)}{p_{[B]}(t)} \right).
\]

We impose the condition of single photon emission by introducing the additional requirement that immediately after emission of a photon the system is projected into the ground state \(|0\rangle\). While \( \langle p(t) \rangle \) and \( \langle p(t + \tau) \rangle \) in Eq. (S2) are given by the time-independent probability \( p_{[B]}(\infty) \) as before, for the numerator in Eq. (S2) we now find

\[
\langle p(t)p(t + \tau) \rangle = \langle p_{[B]}(t) \cdot p_{[0] \rightarrow [B]}(t + \tau|t) \rangle = \langle p_{[B]}(t) \cdot p_{[0] \rightarrow [B]}(\tau) \rangle = p_{[B]}(\infty) \cdot p_{[0] \rightarrow [B]}(\tau),
\]

where \( p_{[0] \rightarrow [B]}(t + \tau|t) \) is the probability to find the system in state \(|0\rangle\) at time \( t \) and in state \(|B\rangle\) at time \( t + \tau \) and \( p_{[0] \rightarrow [B]}(\tau) \) is the probability for a transition from \(|0\rangle\) to \(|B\rangle\) after time \( \tau \). By solving the differential Eq. (S6) we find \( p_{[B]}(\infty) = \gamma_{abs}/(\gamma_{abs} + \gamma_{rad}) \) and \( p_{[0] \rightarrow [B]}(\tau) = \gamma_{abs}/(\gamma_{abs} + \gamma_{rad}) \cdot (1 - \exp[-(\gamma_{abs} + \gamma_{rad})|\tau|]) \) and with the abbreviation \( \tau_0 = 1/(\gamma_{abs} + \gamma_{rad}) \) we find the result of Hofmann et al.\(^5\) for single-photon emission from CNTs,

\[
g^{(2)}(\tau) = 1 - e^{-(\gamma_{abs} + \gamma_{rad})|\tau|} = 1 - e^{-|\tau|/\tau_0}.
\]

To formulate a model that captures both bunching due to PL intermittence and antibunching due to single-photon emission, we finally consider \( g^{(2)}(\tau) \) given by the product of (S8) and (S5). In order to describe imperfect antibunching given by \( g^{(2)}(0) > 0 \), we also multiply \( \exp[-|\tau|/\tau_0] \) with an additional factor \( \eta \leq 1 \) and reproduce the result of Walden-Newman et al.\(^8\) for single-photon emission from spectrally diffusing CNTs,

\[
g^{(2)}(\tau) = \left( 1 - \eta \cdot e^{-|\tau|/\tau_0} \right) \left( 1 + \frac{\tau_d}{\tau_s} e^{-\left(\frac{\tau_s}{\tau_d} + \frac{\tau_d}{\tau_s}\right)|\tau|} \right).
\]
This derivation no longer yields the correct result when the implicit assumption $\gamma_{\text{abs}} \gg \gamma_{\text{rad}}$ is relaxed, since the formal decoupling of both two-level sub-systems in Fig. S2 is lost. A more general treatment shows, however, that Eq. (S9) still holds to lowest order in $\kappa/\gamma$, when $\tau_s = (\gamma_{\text{abs}} + \gamma_{\text{rad}})/(\gamma_{\text{abs}} \cdot \kappa_s)$ is used instead of $\tau_s = 1/\kappa_s$. This modification can be interpreted as the introduction of an effective shelving time that takes into account that the shelving state $|D\rangle$ is not directly accessible from the ground state $|0\rangle$ by weighting $1/\kappa_s$ with the occupation probability $\gamma_{\text{abs}}/(\gamma_{\text{abs}} + \gamma_{\text{rad}})$ of the excited state $|B\rangle$.

From $\gamma_{\text{abs}}, \gamma_{\text{rad}} \gg \kappa_s, \kappa_d$ it follows that $\tau_s, \tau_d \gg \tau_0$, whereby the second term in Eq. (S9) acts like an envelope function, and we define $g_{\text{max}}^{(2)} = 1 + \kappa_s/\kappa_d$ as its maximum value at $\tau = 0$. We note that the value of $g_{\text{max}}^{(2)}$ is a measure of the degree of banching. When $\kappa_s > \kappa_d$, banching is predominant in the sense that the emitter spends more time in the dark state than in the bright state, and this scenario is captured by $g_{\text{max}}^{(2)} > 2$. On the other hand, for $g_{\text{max}}^{(2)} < 2$ the emitter spends more time in the bright state than in the dark state. Whereas in the absence of PL intermittence the condition $g^{(2)}(0) < 0.5$ is considered an evidence for single photon emission, this requirement is not applicable in the presence of blinking due to the multiplication with the second term in (S9). Instead, the degree of correlation $\eta$ should be considered, which can be calculated as $\eta = 1 - g^{(2)}(0)/g_{\text{max}}^{(2)}$, and the condition $\eta > 0.5$ is indicative of single photon emission.

As a first example, we apply Eq. (S9) to auto-correlation measurements of $E_{11}$ in Fig. S3. While bunching is generally present for all $E_{11}$ auto-correlation measurements, we observe $E_{11}$ emission showing no (Fig. S3a), weak (Fig. S3b) or moderate (Fig. S3c) antibunching, indicative of different degrees of exciton localization.

To proceed, we show fits according to Eq. (S9) to the normalized coincidence counts $g^{(2)}(\tau)$ for CNTs A and B from the main text in Fig. S4a-d (left and right columns, respectively). From these fits we determine the degree of correlation $\eta$ (noted in the top right respective corners of Fig. S4a-d), the time constant $\tau_0$, the shelving time $\tau_s$, and the deshelving time $\tau_d$.

Applying this procedure to all CNTs of our study, we find $\tau_0 \ll \tau_s, \tau_d$ (data not shown), verifying the previous assumption $\gamma_{\text{abs}}, \gamma_{\text{rad}} \gg \kappa_s, \kappa_d$. Furthermore, in a plot of deshelving time $\tau_d$ against shelving time $\tau_s$ (Fig. S4e) for X and T (green and red data points, respectively) the data scatters around the solid gray line of equal time scales and mostly falls within the gray shaded area corresponding to values between 1/2 and 2 for $\tau_s/\tau_d$. We can therefore replace shelving and deshelving time by a single blinking time $\tau_{\text{blink}}$ and investigate its dependence on the detuning between $E_{11}$ and the excitation laser energy. Fig. S4f shows the results for X and T auto-correlations (green and red data points, respectively) together with the center-of-mass for three groups of data points around 0, 70 and 190 meV detuning (black diamonds). We observe an increase of the blinking time with increasing laser detuning and discuss in the following how this finding can be explained by a variation of the rate $\gamma_{\text{abs}}$.

Since in the main text $\gamma_{\text{abs}}$ was introduced as an effective rate capturing the actual excitation path via relaxation from a higher
energy state, this rate is expected to decrease with increasing detuning due to a less efficient relaxation mechanism with growing energy mismatch. We quantify this increase by finding a confidence interval for $\gamma_{\text{abs}}$ by employing an affine invariant Markov chain Monte Carlo ensemble sampler\(^7,^8\) for the fits of Eq. (S9). Indeed, we observe a decrease of $\gamma_{\text{abs}}$ by a factor of 1.5 when assuming the range 39–91 ns for $\gamma_{\text{blinking}}$ given by the three-center-of-mass points introduced in Fig. S4f.

Interestingly, we found no obvious dependence of the blinking time on the excitation power (see Fig. S13). This finding proves that the microscopic origin of the PL intermittence is different in CNTs than in self-assembled quantum dots, where substantial power dependence has been observed.\(^9,^10\) This may indicate that in CNTs the relaxation from higher energy states is a time-limiting factor which determines the effective rate $\gamma_{\text{abs}}$.

III. Blinking single-photon source with two competing emissive states

The scenario discussed in the main text, where $T$ is the negatively charged counterpart of $X$, and emission from $X$ and $T$ is mutually exclusive, is formulated in terms of the level scheme in Fig. S5. The system is assumed to exhibit switching between a neutral state (left hand side) and a negatively charged state (right hand side) with rates $\kappa_{\text{XT}}$, $\kappa_{\text{TX}}$, respectively. In the neutral state, emission from the trap state is attributed to $X$, while in the negatively charged state, emission from the trap state is attributed to $T$. In addition, the ground state $|0\rangle$ and the exciton continuum state $|E_{11}\rangle$ are split into two respective states $|0\rangle_X$, $|0\rangle_T$ and $|E_{11}\rangle_X$, $|E_{11}\rangle_T$ of different charge, in order to support a “memory” of the current trap charge state, even if the trap state is not occupied. For brevity, this model of mutual exclusive emission will be called ME model in the following.

For numerical analysis, we formulate the master equation as follows:

$$\frac{d}{dt}\begin{pmatrix} p_{|0\rangle_X}(t) \\ p_{|0\rangle_T}(t) \\ p_{|E_{11}\rangle_X}(t) \\ p_{|E_{11}\rangle_T}(t) \\ p_{|X\rangle}(t) \\ p_{|T\rangle}(t) \end{pmatrix} = \begin{pmatrix} -\gamma_{\text{abs}} - \kappa_{\text{XT}} & \kappa_{\text{TX}} & \gamma_{11} & 0 & \gamma_{X} & 0 \\ \kappa_{\text{XT}} & -\gamma_{\text{abs}} - \kappa_{\text{TX}} & 0 & \gamma_{11} & 0 & \gamma_{T} \\ \gamma_{\text{abs}} & 0 & -\gamma_{11} - \kappa_{\text{XT}} - \kappa_{\text{X}} & \kappa_{\text{TX}} & 0 & 0 \\ 0 & \gamma_{\text{abs}} & \kappa_{\text{X}} & -\gamma_{11} - \kappa_{\text{TX}} - \kappa_{\text{X}} & 0 & 0 \\ 0 & 0 & 0 & \kappa_{\text{TX}} & 0 & -\gamma_{T} \\ 0 & 0 & 0 & 0 & \kappa_{\text{X}} & 0 \end{pmatrix} \begin{pmatrix} p_{|0\rangle_X}(t) \\ p_{|0\rangle_T}(t) \\ p_{|E_{11}\rangle_X}(t) \\ p_{|E_{11}\rangle_T}(t) \\ p_{|X\rangle}(t) \\ p_{|T\rangle}(t) \end{pmatrix}.$$  \hspace{1cm} (S10)

We use Eq. (S2) to derive expressions for the normalized coincidence counts $g^{(2)}_{XX}(\tau)$, $g^{(2)}_{TT}(\tau)$ and $g^{(2)}_{XT}(\tau)$ for the auto-correlation of $X$ and $T$ as well as the cross-correlation of $X$ and $T$, respectively, to obtain:

$$g^{(2)}_{XX}(\tau) = \frac{\langle p_{|X\rangle}(t)p_{|X\rangle}(t+\tau) \rangle}{\langle p_{|X\rangle}(t) \rangle \langle p_{|X\rangle}(t+\tau) \rangle}, \quad g^{(2)}_{TT}(\tau) = \frac{\langle p_{|T\rangle}(t)p_{|T\rangle}(t+\tau) \rangle}{\langle p_{|T\rangle}(t) \rangle \langle p_{|T\rangle}(t+\tau) \rangle}, \quad g^{(2)}_{XT}(\tau) = \frac{\langle p_{|X\rangle}(t)p_{|T\rangle}(t+\tau) \rangle}{\langle p_{|X\rangle}(t) \rangle \langle p_{|T\rangle}(t+\tau) \rangle}.$$  \hspace{1cm} (S11)

As before, we find $\langle p_{|\psi\rangle}(t) \rangle = p_{|\psi\rangle}(\infty)$ and $\langle p_{|\phi\rangle}(t+\tau) \rangle = p_{|\phi\rangle}(\infty)$ in the steady state limit and implement single photon emission by the assumption that the system is projected into the ground state upon photon emission. We calculate

$$\langle p_{|\psi\rangle}(t)p_{|\phi\rangle}(t+\tau) \rangle = \langle p_{|\psi\rangle}(t)p_{|0(\psi)\rangle\rightarrow|\phi\rangle}(t+\tau|t) \rangle = \langle p_{|\psi\rangle}(t) \cdot p_{|0(\psi)\rangle\rightarrow|\phi\rangle}(\tau) \rangle = p_{|\psi\rangle}(\infty) \cdot p_{|0(\psi)\rangle\rightarrow|\phi\rangle}(\tau),$$  \hspace{1cm} (S12)

where $|0(\psi)\rangle$ is the ground state that the system is projected into after the emission of a photon from state $|\psi\rangle$, $p_{|X\rangle\rightarrow|\phi\rangle}(t+\tau|t)$ is the probability to find the system in state $|\chi\rangle$ at time $t$ and in state $|\phi\rangle$ at time $t+\tau$, and $p_{|X\rangle\rightarrow|\phi\rangle}(\tau)$ is the probability for a
transition from $|\chi\rangle$ to $|\phi\rangle$ after time $\tau$. Combining these results with Eq. (S11) we obtain:

$$g_{XX}^{(2)}(\tau) = \frac{p_{|0\rangle_X \rightarrow |X\rangle}^{(2)}(\tau)}{p_{|X\rangle}^{(2)}(\tau)}, \quad g_{TT}^{(2)}(\tau) = \frac{p_{|0\rangle_T \rightarrow |T\rangle}^{(2)}(\tau)}{p_{|T\rangle}^{(2)}(\tau)}, \quad g_{XT}^{(2)}(\tau) = \frac{p_{|0\rangle_X \rightarrow |T\rangle}^{(2)}(\tau)}{p_{|T\rangle}^{(2)}(\tau)}.$$  \hspace{1cm} (S13)

To calculate the probabilities of the form $p_{|\psi\rangle}^{(2)}(\infty)$ and $p_{|\phi\rangle}^{(2)}(\tau)$ we use the fact that solutions of Eq. (S10) can be expressed using the matrix exponential $\exp(A)$ as $p_{\text{ME}}(t) = \exp(t \cdot A_{\text{ME}}) \cdot p_{\text{ME}}(0)$. By choosing a suitable initial condition $p_{\text{ME}}(0)$ of the form $(0, 0, 0, 0, 0, \ldots , 0)$ this allows for direct numerical calculation of $p_{|\phi\rangle}^{(2)}(\tau)$, while $p_{|\psi\rangle}^{(2)}(\infty)$ can be found from

$$\lim_{t \rightarrow \infty} \exp(t \cdot A_{\text{ME}}).$$

Any rate model that is solved using this approach yields perfect antibunching, since it is introduced by the assumption that after the emission of a photon the system is instantaneously projected into the ground state. For experimental data, however, this is generally not the case, mainly due to finite bin width of time-correlation steps or due to a stray background signal. To include the possibility of imperfect antibunching in our models, we consider an additional uncorrelated background signal. We start from the second order correlation function

$$g^{(2)}(\tau) = \frac{\langle I_1(t)I_2(t+\tau) \rangle}{\langle I_1(t) \rangle \langle I_2(t+\tau) \rangle},$$  \hspace{1cm} (S14)

where $I_1(t)$ and $I_2(t)$ are the time-dependent emission intensities in two (possibly identical) spectral bands 1 and 2. We decompose each intensity $I_i(t)$ into a contribution $I_{i|}^{(2)}(t)$ from an emitter state $|i\rangle$ and a time-independent background intensity $I_i^{(B)}$ by writing $I_i(t) = I_{i|}^{(2)}(t) + I_i^{(B)}$ and obtain:

$$g^{(2)}(\tau) = \frac{\langle I_{1|}^{(2)}(t)I_{2|}^{(2)}(t+\tau) + I_i^{(B)} \rangle}{\langle I_{1|}^{(2)}(t) \rangle \langle I_{2|}^{(2)}(t+\tau) \rangle} = \frac{\langle I_{1|}^{(2)}(t)I_{2|}^{(2)}(t+\tau) \rangle}{\langle I_{1|}^{(2)}(t) \rangle \langle I_{2|}^{(2)}(t+\tau) \rangle} + \frac{I_i^{(B)} \langle I_{1|}^{(2)}(t+\tau) \rangle}{\langle I_{1|}^{(2)}(t) \rangle \langle I_{2|}^{(2)}(t+\tau) \rangle},$$  \hspace{1cm} (S15)

where $I_{1|}^{(2)}$ and $I_{2|}^{(2)}$ are the time-averages of the time-dependent intensities $I_{1|}^{(2)}(t)$ and $I_{2|}^{(2)}(t)$, respectively. By introducing the “pure” second order correlation function of the emitter without background signal,

$$g_{\text{pure}}^{(2)}(\tau) = \frac{\langle I_{1|}^{(2)}(t)I_{2|}^{(2)}(t+\tau) \rangle}{\langle I_{1|}^{(2)}(t) \rangle \langle I_{2|}^{(2)}(t+\tau) \rangle} = \frac{\langle I_{1|}^{(2)}(t)I_{2|}^{(2)}(t+\tau) \rangle}{I_{1|}^{(2)}I_{2|}^{(2)}},$$  \hspace{1cm} (S16)

the above can be rewritten as

$$g^{(2)}(\tau) = \frac{I_{1|}^{(2)}I_{2|}^{(2)}}{\langle I_{1|}^{(2)} \rangle \langle I_{2|}^{(2)} \rangle} g_{\text{pure}}^{(2)}(\tau) + \frac{I_{1|}^{(2)}I_{2|}^{(2)}}{\langle I_{1|}^{(2)} \rangle \langle I_{2|}^{(2)} \rangle} \frac{I_{1|}^{(B)}I_{2|}^{(B)}}{\langle I_{1|}^{(2)} \rangle \langle I_{2|}^{(2)} \rangle} + \frac{I_{1|}^{(B)}I_{2|}^{(B)}}{\langle I_{1|}^{(2)} \rangle \langle I_{2|}^{(2)} \rangle}.$$  \hspace{1cm} (S17)

By defining the background intensity ratios $\zeta_1 = \frac{I_{1|}^{(B)}}{I_{1|}}$ and $\zeta_2 = \frac{I_{2|}^{(B)}}{I_{2|}}$ we finally calculate

$$g^{(2)}(\tau) = \frac{1}{(1 + 1/\zeta_1)(1 + 1/\zeta_2)} \cdot g_{\text{pure}}^{(2)}(\tau) + \frac{1}{(1 + 1/\zeta_1)(1 + 1/\zeta_2)} + \frac{1}{1 + \zeta_1}. \hspace{1cm} (S18)$$

We illustrate the limits of the ME model by showing its failure to reproduce the data of CNT A from the main text. In Fig. 6S6, the solid lines show plots of $g^{(2)}(\tau)$ obtained by substituting $g_{XX}^{(2)}(\tau)$, $g_{TT}^{(2)}(\tau)$ and $g_{XT}^{(2)}(\tau)$ from Eq. (S13) for $g_{\text{pure}}^{(2)}(\tau)$ in Eq. (S18) and introducing two background intensity ratios $\zeta_X$ and $\zeta_T$ for the spectral bands of X and T, respectively. In the top row of Fig. 6S6 a fitting procedure was used to find the best fit of $g^{(2)}(\tau)$ to the auto-correlation data of X (light green), thereby fixing all parameters in Eqs. (S10) and (S18) except $\gamma_T$, $\kappa_T$ and $\zeta_T$. By varying only these three remaining parameters, however, the resulting functional dependencies of $g_{XX}^{(2)}(\tau)$ and $g_{XT}^{(2)}(\tau)$ were unable to reproduce the auto-correlation data of T (light red) and the cross-correlation data of X and T (orcid) as shown for an exemplary set of rates #1 in Fig. 6S6 and c. In a complementary way, in the bottom row of Fig. 6S6, a fitting procedure was used to find the best fit of $g^{(2)}(\tau)$ to the auto-correlation data of T (light red). As before, a variation of the still undetermined parameters $\gamma_X, \kappa_X$ and $\chi_X$ could not reproduce the auto-correlation data of X (light green) and the cross-correlation data of X and T (orcid) as shown for a set of rates #2 in Fig. 6S6 and f.

From a closer inspection of the level scheme in Fig. 6S5 we determine the origin of the failure to reproduce the data in Fig. 6S6 and show that the ME model is conceptually unable to explain our measurements. For the auto-correlation of X and T we observe a contrasting behavior for the functional form of $g^{(2)}(\tau)$ in Fig. 6S6a, b and c: if $g^{(2)}(\tau)$ well reproduces the bunching behavior for the auto-correlation of X, it falls short to do so for the auto-correlation of T (black curve too flat in Fig. 6S6b) and vice versa.
as shelving state and constitutes the origin of PL intermittence. We begin with a model where only a single defect site is present in the vicinity of zero time delay, whereas instead of a global blinking behavior is to be expected. This finding is in agreement with earlier reports on competing emission from two different emissive states.

As an alternative to the ME model we introduce the model discussed in the main text, where an additional dark state |D⟩ acts as shelving state and constitutes the origin of PL intermittence. We begin with a model where only a single defect site is present (Fig. S7), for brevity termed model DS1, to fit the data with pronounced bunching and antibunching in the cross-correlation of X and T. From the level scheme, we derive the master equation

\[
\frac{d}{dt} \begin{pmatrix} p_{\{0\}}(t) \\ p_{\{E_{11}\}}(t) \\ p_{\{|D\}\}(t) \\ p_{\{|X\}\}(t) \\ p_{\{|T\}\}(t) \end{pmatrix} = A_{DS1} \begin{pmatrix} p_{\{0\}}(t) \\ p_{\{E_{11}\}}(t) \\ p_{\{|D\}\}(t) \\ p_{\{|X\}\}(t) \\ p_{\{|T\}\}(t) \end{pmatrix}.
\]

(S19)

In summary, the ME model is unable to reproduce our measurement results for the cross-correlation of X and T. In addition, for all emitters with strong bunching in the auto-correlation of X and T indicated by \(g^{(2)}_{\text{max}} > 2\), the ME model also fails to explain the auto-correlation data. We conclude that the ME model is conceptually inapt to explain our observations.

IV. Emission from a single defect site in the presence of a dark state

As an alternative to the ME model we introduce the model discussed in the main text, where an additional dark state |\text{D}\rangle acts as shelving state and constitutes the origin of PL intermittence. We begin with a model where only a single defect site is present (Fig. S7), for brevity termed model DS1, to fit the data with pronounced bunching and antibunching in the cross-correlation of X and T. From the level scheme, we derive the master equation

\[
\frac{d}{dt} \begin{pmatrix} p_{\{0\}}(t) \\ p_{\{E_{11}\}}(t) \\ p_{\{|D\}\}(t) \\ p_{\{|X\}\}(t) \\ p_{\{|T\}\}(t) \end{pmatrix} = A_{DS1} \begin{pmatrix} p_{\{0\}}(t) \\ p_{\{E_{11}\}}(t) \\ p_{\{|D\}\}(t) \\ p_{\{|X\}\}(t) \\ p_{\{|T\}\}(t) \end{pmatrix}.
\]

(S19)

For the cross-correlation of X and T, the ME model fails to explain the occurrence of bunching combined with antibunching on a shorter timescale, but instead shows a too broad antibunching dip and no bunching (Fig. S6c and f). This feature is intuitively understandable by the observation that bunching in cross-correlation is caused by PL intermittence of both X and T, which cannot be accounted for by the assumption of mutually exclusive emission, where a mere switching between X and T instead of a global blinking behavior is to be expected. This finding is in agreement with earlier reports on competing emission from two different emissive states.\(^{10–13}\)

In particular we find that the auto-correlation data of both X and T assume values greater than 2 in the vicinity of zero time delay, whereas \(g^{(2)}_{\text{max}} > 2\) is only possible for the auto-correlation of either X or T in the framework of the ME model. Turning back to the definition \(g^{(2)}_{\text{max}} = 1 + \kappa_{\text{a}} / \kappa_{\text{d}}\) this observation is readily understood: since blinking in the ME model is explained by the mutual exclusiveness of emission from X and T, the ratios of shelving and desheling rate \(\kappa_{\text{a}} / \kappa_{\text{d}}\) from the perspective of X and T are the inverse of each other. Consequently, \(g^{(2)}_{\text{max}} > 2\) for X automatically implies \(g^{(2)}_{\text{max}} < 2\) for T and vice versa.

In summary, the ME model is unable to reproduce our measurement results for the cross-correlation of X and T. In addition, for all emitters with strong bunching in the auto-correlation of X and T indicated by \(g^{(2)}_{\text{max}} > 2\), the ME model also fails to explain the auto-correlation data. We conclude that the ME model is conceptually inapt to explain our observations.

IV. Emission from a single defect site in the presence of a dark state

As an alternative to the ME model we introduce the model discussed in the main text, where an additional dark state |\text{D}\rangle acts as shelving state and constitutes the origin of PL intermittence. We begin with a model where only a single defect site is present (Fig. S7), for brevity termed model DS1, to fit the data with pronounced bunching and antibunching in the cross-correlation of X and T. From the level scheme, we derive the master equation

\[
\frac{d}{dt} \begin{pmatrix} p_{\{0\}}(t) \\ p_{\{E_{11}\}}(t) \\ p_{\{|D\}\}(t) \\ p_{\{|X\}\}(t) \\ p_{\{|T\}\}(t) \end{pmatrix} = A_{DS1} \begin{pmatrix} p_{\{0\}}(t) \\ p_{\{E_{11}\}}(t) \\ p_{\{|D\}\}(t) \\ p_{\{|X\}\}(t) \\ p_{\{|T\}\}(t) \end{pmatrix}.
\]

(S19)
Figure S7. Level scheme used to model a single defect site in the presence of a dark state: ground state |0\rangle, exciton continuum |E_{11}\rangle, localized states |X\rangle and |T\rangle, and dark state |D\rangle with their corresponding rates.

Figure S8. Normalized coincidence counts $g^{(2)}(\tau)$ for auto-correlation of X (light green) and T (light red) as well as cross-correlation of X and T (orchid) for CNT A from the main text. Fits to $g^{(2)}(\tau)$ were obtained with the DS1 model (solid lines) and resulted in the values $\gamma_{11} = 4.2 \times 10^{10}$ s$^{-1}$, $\kappa_X = 4.0 \times 10^{10}$ s$^{-1}$, $\kappa_T = 1.5 \times 10^{11}$ s$^{-1}$, $\gamma_X = 2.0 \times 10^9$ s$^{-1}$, $\gamma_T = 2.0 \times 10^9$ s$^{-1}$, $\kappa_d = 1.0 \times 10^7$ s$^{-1}$, $\zeta_X = 1.9$ and $\zeta_T = 2.1$. The fits were found to depend only on the effective transition rate from $|0\rangle$ to $|D\rangle$, leaving freedom for the individual values of $\gamma_{abs}$ and $\kappa_a$. Choosing $\gamma_{abs} = 1.0 \times 10^8$ s$^{-1}$ resulted in the best-fit value $\kappa_a = 1.4 \times 10^{13}$ s$^{-1}$.

In the same way as before we use the solution $p_{DS1}(t) = \exp(t \cdot A_{DS1}) \cdot p_{DS1}(0)$ of the master equation to find numerical expressions for the normalized coincidence counts

$$
g^{(2)}_{XX}(\tau) = \frac{p_{|0\rangle \rightarrow |X\rangle}(\tau)}{p_{|X\rangle}(\infty)}, \quad g^{(2)}_{TT}(\tau) = \frac{p_{|0\rangle \rightarrow |T\rangle}(\tau)}{p_{|T\rangle}(\infty)}, \quad g^{(2)}_{XT}(\tau) = \frac{p_{|0\rangle \rightarrow |T\rangle}(\tau)}{p_{|T\rangle}(\infty)}
$$

(S20)

derived by calculations similar to Eqs. (S11) to (S13). We also follow Eqs. (S15) to (S18) and write

$$
g^{(2)}(\tau) = \frac{1}{(1 + 1/\zeta_1)(1 + 1/\zeta_2)} \cdot g^{(2)}_{pure}(\tau) + \frac{1}{(1 + 1/\zeta_1)(1 + \zeta_2)} + \frac{1}{1 + \zeta_1}
$$

(S21)

with the background intensity ratios $\zeta_1 = I_{1|\gamma_1}/I_T^B$ and $\zeta_2 = I_{2|\gamma_2}/I_T^B$ in two (possibly identical) spectral bands 1 and 2, to account for imperfect antibunching.

We obtain fits to the data of CNT A from the main text by substituting $g^{(2)}_{pure}(\tau)$ with $g^{(2)}_{XX}(\tau)$, $g^{(2)}_{TT}(\tau)$ and $g^{(2)}_{XT}(\tau)$ and introducing two background intensity ratios $\zeta_X$ and $\zeta_T$ for the spectral bands of X and T. This choice allows to fix all rates in the model as well as $\zeta_X$ and $\zeta_T$ by fitting the auto-correlation of X and T, and to subsequently test the model by comparing the cross-correlation of X and T with the resulting functional dependency of $g^{(2)}_{XT}(\tau)$. As a representative for the class of CNTs with pronounced bunching and antibunching in the cross-correlation of X and T, we plot the auto-correlation of X (light green) and T (light red) as well as the cross-correlation of X and T (orchid) of CNT A from the main text in Fig. S8. The solid lines show the resulting functional dependencies of $g^{(2)}(\tau)$ according to the DS1 model using the fitting method described above. We emphasize the good agreement between model fit and data obtained without additional parameters for the cross-correlation of X and T in Fig. S8c.
Figure S9. Simplified sketch of the level scheme used to model a double defect site in the presence of a dark state. The charge states of the left and the right defect site change with rates $\Gamma_L$ and $\Gamma_R$, respectively, and transitions into equal charge states of both traps are suppressed by a factor $\varepsilon < 1$. For each charge configuration we consider the ground state $|0\rangle$, the exciton continuum $|E_{11}\rangle$, the localized states of left ($|X\rangle_L$ or $|T\rangle_L$) and right ($|X\rangle_R$ or $|T\rangle_R$) defect site and the dark state $|D\rangle$ with their corresponding rates.

V. Emission from two correlated defect sites in the presence of a dark state

To explain the data with weak bunching and antibunching in the cross-correlation of $X$ and $T$, we extend the model DS1 by the introduction of a second defect site. In order to preserve pronounced antibunching in the auto-correlation of $X$ and $T$, we further assume that the two defect sites are favored to be in opposite charge states. For brevity, this model is termed DS2 in the following.

While the level scheme in Fig. 4e in the main text illustrates this behavior, a theoretical description of the DS2 model requires a “memory” of the charge state of both defect sites, even if they are not occupied. A suitable level scheme including this feature is shown in Fig. S9, where a left and a right defect site, $L$ and $R$, are considered. The two traps change their charge state with rates $\gamma_X$ and $\gamma_T$, respectively, and transitions into equal charge states of both traps are suppressed by a factor $\varepsilon < 1$. For fixed charges, the dynamics of the two defect sites are equivalent to the dynamics in Fig. S7. Excitation and decay of $E_{11}$ occur with rates $\gamma_{abs}$ and $\gamma_{11}$, where $i$ is either $L$ (left trap) or $R$ (right trap). The trap states are populated with rates $\kappa_X^s$ or $\kappa_T^s$ and decay with rate $\gamma_X^s$ or $\gamma_T^s$ depending on the current charge state. The dark state $|D\rangle$ is populated with rate $\kappa_d^s$ and depopulated with rate $\kappa_d^d$.

While the numerical solution of the rate model corresponding to this level scheme is conceptually identical to the solutions found for models ME and DS1, there are 64 possible states to be considered making a more structured approach necessary. We start by writing down a master equation for the left defect site as a function of the charge state $\chi_L$.

\[
\frac{d}{dt} \left( \begin{array}{c} p_{|0\rangle_L}(t) \\ p_{|E_{11}\rangle_L}(t) \\ p_{|D\rangle_L}(t) \\ p_{|A(\chi_L)\rangle_L}(t) \end{array} \right) = \left( \begin{array}{cccc} -\gamma_{abs} & \gamma_{11} & 0 & 0 \\ \gamma_{abs} & -\gamma_{11} - \kappa_X^L - \kappa_X^{(\chi_L)} & \gamma_X^L & 0 \\ 0 & \kappa_X^L & -\kappa_d^L & 0 \\ 0 & \kappa_X^{(\chi_L)} & 0 & -\gamma_{11} \end{array} \right) \left( \begin{array}{c} p_{|0\rangle_L}(t) \\ p_{|E_{11}\rangle_L}(t) \\ p_{|D\rangle_L}(t) \\ p_{|A(\chi_L)\rangle_L}(t) \end{array} \right),
\]

where $|\Lambda(\chi_L)\rangle_L$ is the charge configuration of the left localized state depending on the charge state $\chi_L$ of the left defect site, i.e. $|\Lambda(0)\rangle_L = |X\rangle_L$ and $|\Lambda(-)\rangle_L = |T\rangle_L$. As a next step, we formulate a rate equation for both defect sites as a function of the
charge states $\chi_R$ of the right defect site and $\chi_L$ of the left defect site. We obtain
\[
\frac{d}{dt} r(\chi_R, \chi_L, t) = \begin{pmatrix}
L(\chi_L) - \gamma_{\text{abs}}^R I_4 \\
\gamma_{\text{abs}}^R I_4 \\
0_4 \\
0_4
\end{pmatrix}
\begin{pmatrix}
\gamma_{\text{abs}}^R I_4 \\
L(\chi_L) - (\gamma_{11}^R + \kappa_s^R + \kappa_{\Lambda(\chi_R)}^R) I_4 \\
\kappa_s^R I_4 \\
\kappa_{\Lambda(\chi_R)}^R I_4
\end{pmatrix}
\begin{pmatrix}
0_4 \\
0_4 \\
0_4 \\
0_4
\end{pmatrix}
\begin{pmatrix}
\gamma_{\Lambda(\chi_R)}^R I_4 \\
L(\chi_L) - \gamma_{\text{abs}}^R I_4 \\
0_4 \\
0_4
\end{pmatrix}
\begin{pmatrix}
r(\chi_R, \chi_L, t)
\end{pmatrix},
\]
where
\[
r(\chi_R, \chi_L, t) = \begin{pmatrix}
p_{(0, R)}(t) \cdot I(\chi_L, t) \\
p_{(E_{11}, R)}(t) \cdot I(\chi_L, t) \\
p_{(D, R)}(t) \cdot I(\chi_L, t) \\
p_{(\Lambda(\chi_R))s}(t) \cdot I(\chi_L, t)
\end{pmatrix},
\]
$I_4$ is a $4 \times 4$ identity matrix, $0_4$ is a $4 \times 4$ zero matrix and $|\Lambda(\chi_R))_R$ is the charge configuration of the right localized state depending on the charge state $\chi_R$ of the right defect site, i.e. $|\Lambda(0))_R = |X)_R$ and $|\Lambda(\text{-})_R = |T)_R$.

Finally, we need to combine the differential equation for $r(\chi_R, \chi_L, t)$ with the charging and discharging dynamics of the two defect sites. In order not to further increase complexity, we choose the simplest approach here, where the corresponding rates are independent of the occupation of the defect site, and obtain the master equation
\[
\frac{d}{dt} p_{\text{DS2}}(t) = A_{\text{DS2}} \cdot p_{\text{DS2}}(t),
\]
where
\[
A_{\text{DS2}} = \begin{pmatrix}
R(0, 0) - (\Gamma_R + \Gamma_L) I_{16} \\
\Gamma_R I_{16} \\
\Gamma_L I_{16} \\
0_{16}
\end{pmatrix}
\begin{pmatrix}
\varepsilon \Gamma_R I_{16} \\
0_{16} \\
\varepsilon \Gamma_L I_{16} \\
0_{16}
\end{pmatrix}
\begin{pmatrix}
\varepsilon \Gamma_R I_{16} \\
0_{16} \\
\varepsilon \Gamma_L I_{16} \\
0_{16}
\end{pmatrix}
\begin{pmatrix}
0_{16} \\
\Gamma_R I_{16} \\
\Gamma_L I_{16} \\
0_{16}
\end{pmatrix}
\begin{pmatrix}
R(0, -) - \varepsilon (\Gamma_R + \Gamma_L) I_{16} \\
0_{16} \\
\varepsilon \Gamma_R I_{16} \\
\varepsilon \Gamma_L I_{16}
\end{pmatrix}
\begin{pmatrix}
0_{16} \\
\Gamma_R I_{16} \\
\Gamma_L I_{16} \\
0_{16}
\end{pmatrix}
\begin{pmatrix}
R(-, -) - (\Gamma_R + \Gamma_L) I_{16}
\end{pmatrix},
\]
and
\[
p_{\text{DS2}}(t) = \begin{pmatrix}
r(0, 0, t) \\
r(-, 0, t) \\
r(0, -, t) \\
r(-, -, t)
\end{pmatrix},
\]
$I_{16}$ is a $16 \times 16$ identity matrix and $0_{16}$ is a $16 \times 16$ zero matrix. In order to calculate
\[
g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle} = \frac{\langle p(t)p(t+\tau) \rangle}{\langle p(t) \rangle \langle p(t+\tau) \rangle},
\]
as derived in (S2), it is now important to observe that there are different states in the system that contribute to the emission in the X and T spectral bands. In a measurement of $g^{(2)}(\tau)$, time correlations between start and stop events are performed. We can therefore express the probabilities in Eq. (S28) by summing over possible initial and final states $|i\rangle$ and $|f\rangle$ and obtain

$$\langle p(t) \rangle = \sum_{|i\rangle} p_{|i\rangle}(\infty)$$  \hspace{1cm} (S29)

and

$$\langle p(t + \tau) \rangle = \sum_{|f\rangle} p_{|f\rangle}(\infty),$$  \hspace{1cm} (S30)

where the sums run over all initial and final states that contribute to the emission in the respective spectral bands. In a similar way, the numerator in (S28) can be written as

$$\langle p(t)p(t + \tau) \rangle = \sum_{|i\rangle} \sum_{|f\rangle} p_{|i\rangle}(\infty) \cdot p_{|0(i)\rangle \rightarrow |f\rangle}(\tau),$$  \hspace{1cm} (S31)

where $|0(i)\rangle$ is the ground state that the system is projected into after emission from the state $|i\rangle$. Note that $|0(i)\rangle$ is not necessarily unique. For example, if both trap states are in state $|X\rangle$, then after emission of a photon in the spectral band of X it is undetermined whether the left or the right defect site has been projected into the corresponding ground state. So, in fact, there is another sum hidden in Eq. (S31) that runs over all possible ground states $|0(i)\rangle$ for any given initial sate $|i\rangle$.

Finally, in Fig. S10 we compare the fits obtained with the DS1 and the DS2 model for the correlation data of CNT B discussed in the main text as a representative for the class of CNTs with weak bunching and antibunching in the cross-correlation of X and T. For the auto-correlation measurements of X and T we find a comparable fit quality for the DS1 model (solid pink lines) and the DS2 model (solid violet lines) in Fig. S10a and b. For the cross-correlation of X and T (Fig. S10c), however, the DS1 model overestimates both bunching and antibunching (solid pink line), whereas the DS2 model reproduces the data reasonably well (solid violet line).

VI. Bunching and antibunching characteristics in photon correlation spectroscopy

In this section we present plots for the quantities $\eta$ and $g^{(2)}_{\text{max}}$, as defined in section II to reveal possible correlations of these values between the different auto and cross-correlation measurements. First, we consider the degree of correlation $\eta$. According to the models DS1 and DS2, the value of $\eta$ for the auto-correlation of X and T is determined by the ratio of emission intensity to background intensity. Since the spectral bands of X and T are disjoint, we expect no correlation between the value of $\eta$ for the auto-correlation of X and T.

Indeed, the corresponding values scatter in the entire top right quadrant of Fig. S11a, where $\eta > 0.5$ holds for the auto-correlation of both X and T. While the finding $\eta > 0.5$ shows that both X and T are single photon emitters, there is no indication that a high degree of correlation for X also implies a high degree of correlation for T or vice versa. In that case, the data points would follow a diagonal line in Fig. S11a.

![Figure S11. Comparison of the degree of correlation $\eta$ obtained for (a) auto-correlation of X and T, (b) auto-correlation of X and cross-correlation of X and T and (c) auto-correlation of T and cross-correlation of X and T. Dashed lines indicate values of $\eta = 0.5$. Violet data points correspond to $\eta < 0.5$ in the cross-correlation of X and T, while pink data points correspond to $\eta > 0.5$ in the cross-correlation of X and T.](image-url)
Figure S12. Comparison of the bunching amplitude $g_{\text{max}}^{(2)}$ obtained for (a) auto-correlation of X and T, (b) auto-correlation of X and cross-correlation of X and T and (c) auto-correlation of T and cross-correlation of X and T. Solid lines indicate equal values of $g_{\text{max}}^{(2)}$. Violet data points correspond to $\eta < 0.5$ in the cross-correlation of X and T, while pink data points correspond to $\eta > 0.5$ in the cross-correlation of X and T.

When comparing the auto-correlation of X or T with the cross-correlation of X and T, according to the DS1 model a positive correlation for the auto-correlation and the cross-correlation values of $\eta$ is expected, as the emission background from the auto-correlation contributes “half” to the emission background in the cross-correlation. However, in Fig. S11b and c, no such correlation can be observed. Instead, we find data points with $\eta > 0.5$ (pink data points) and $\eta < 0.5$ (violet data points) in the cross-correlation of X and T for any value $\eta$ in the auto-correlation of X or T.

This finding proves that the DS1 model is not applicable to data featuring $\eta < 0.5$ in the cross-correlation of X and T, since the predicted positive correlation for the auto-correlation and the cross-correlation values of $\eta$ is not present in the data. The introduction of the DS2 model, however, resolves this contradiction: in the case where $\eta < 0.5$ in the cross correlation of X and T (violet data points in Fig. S11b and c), the degree of correlation is expected to be mainly governed by the dynamics of the two corresponding charge states. Therefore we also expect no correlation for $\eta$ between the auto-correlation and the cross-correlation measurements.

We also compare the value of $g_{\text{max}}^{(2)}$, measuring the amplitude of bunching, between the auto-correlation of X and T as well as the cross-correlation of X and T. Since the bunching mechanism is attributed to the same dark state $|D\rangle$, we expect equal values for $g_{\text{max}}^{(2)}$ in auto-correlation of X and T. Fig. S12a shows that indeed the data points follow the solid gray line indicating equal time scales.

For the comparison of $g_{\text{max}}^{(2)}$ between the auto-correlation of X or T and the cross-correlation of X and T in Fig. S12b and c we distinguish between $\eta > 0.5$ (pink data points) and $\eta < 0.5$ (violet data points) in cross-correlation. For the case $\eta > 0.5$, according to the DS1 model we similarly expect equal values for $g_{\text{max}}^{(2)}$, which is confirmed by the pink data points in Fig. S12b and c. For $\eta < 0.5$ in the cross-correlation of X and T, however, we observe smaller values for $g_{\text{max}}^{(2)}$ for the cross-correlation of X and T than in the auto-correlation of X or T (violet data points in Fig. S12b and c). This finding can be interpreted within the DS2 model as follows: due to the suppression of equal charging states of the two defect sites in the DS2 model, in the auto-correlation measurements, only one of the two defect sites emits at a time and therefore a single dark state governs the blinking dynamics. In cross-correlation measurement, however, we detect emission from both defect sites at the same time and therefore blinking can be caused by transitions to the dark state $|D\rangle$ along two different paths in the level scheme in Fig. S9. This can be interpreted as uncorrelated evolution of the blinking dynamics, effectively resulting in a less pronounced blinking behavior.

In summary, we find that correlations of $\eta$ and $g_{\text{max}}^{(2)}$ between the different auto and cross-correlation measurements is according to expectations within the DS1 model for emitters with $\eta > 0.5$ in the cross-correlation of X and T. The discrepancies in the case $\eta < 0.5$ can be resolved by the DS2 model, further underlining its accuracy for this class of emitters.

VII. Correlations at different excitation laser powers

Finally, we discuss the dependence of the degrees of bunching and antibunching on the excitation laser power. Fig. S13a-c shows the degree of antibunching $\eta$ as a function of the laser excitation power for X auto-correlation (Fig. S13a), T auto-correlation (Fig. S13b) and the cross-correlation of X and T (Fig. S13c), respectively. In the latter plot, violet and pink data points correspond to $\eta < 0.5$ and $\eta > 0.5$ in the cross-correlation of X and T, respectively. In all three cases no obvious dependence of the degrees of correlation $\eta$ on the excitation power was found, supporting our interpretation of X and T states as quantum-dot-like emitters in linear response. Fig. S13d-f shows the effective shelving rate $\kappa_{\text{eff}}$ (black data points) and the effective desheling rate $\kappa_{\text{d,eff}}$ (gray data points) obtained from fits with Eq. (S9) as a function of the excitation laser power for X auto-correlation (Fig. S13d), T auto-correlation (Fig. S13e) and the cross-correlation of X and T (Fig. S13f). Also this set of data shows no obvious dependence on the excitation power.
Figure S13. (a)-(c) Degree of antibunching $\eta$ as a function of excitation laser power for X auto-correlation (left panel), T auto-correlation (central panel) and X and T cross-correlation (right panel). In (c), violet and pink data correspond to $\eta < 0.5$ and $\eta > 0.5$, respectively. (d)-(f) Effective shelving and desheling rates, $\kappa_s,\text{eff}$ and $\kappa_d,\text{eff}$, obtained from fits with Eq. (S9) and shown in black and grey, respectively, as a function of the excitation laser power for X auto-correlation (left panel), T auto-correlation (central panel) and X and T cross-correlation (right panel).

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