Observation of biexcitons in monolayer WSe$_2$

1. Experimental Methods

a. Sample preparation

The results presented in the main text were obtained from monolayer WSe$_2$ crystals exfoliated onto a silicon substrate covered by a 285-nm thick SiO$_2$ layer. Freely suspended monolayer samples were also examined to assess the influence of the environment and of different dielectric screening on the excitonic states, as discussed below. These samples were prepared by exfoliating on a SiO$_2$/Si substrate that had been lithographically patterned with etched holes of 3-μm diameter. To control the doping level of the sample in other measurements described below, Cr/Au electrodes are deposited onto exfoliated sample on SiO$_2$/Si substrate using e-beam lithography. In these samples, electrostatic gating was achieved by applying a bias voltage between the sample and the Si substrate.

b. Photodoping and reproducibility of fluence-dependent measurement

Photodoping effects are known to occur in TMDC samples prepared as in our studies$^1$. Such possible changes in doping level with laser excitation could complicate interpretation of our fluence dependent measurements. We investigated this effect by examining the relative strength of charged and neutral exciton emission, as well as by following changes in the emission energy of the charged exciton, which is known to be sensitive to the doping level$^2$. We did, in fact, observe a slight photodoping effect for excitation with the 3.06-eV pulsed laser. We saw an increase in relative emission of the charged exciton compared to the neutral species, as well as a shift of about 1 meV in the
trion emission energy compared to the behavior for cw laser excitation at a lower photon energy (1.92 eV). The photodoping effect was, however, essentially saturated at the lowest excitation fluences used in our pulsed laser measurements. This is confirmed by the lack of any shift in the trion emission energy (< 1 meV in Figs. 1a & b of main text) or any meaningful alteration of the ratio of charged to neutral exciton emission (Fig. S1). Thus, there is no appreciable change in doping induced by a variation of the pump laser fluence, which is the critical question for analysis of our fluence dependence. We also confirmed the unimportance of photodoping in our measurements by collecting identical data for either increasing or decreasing laser fluence.

**c. Laser heating**

The laser pump radiation could, in principle, also give rise to heating, either as a cumulative effect or as a transient response from a single excitation pulse. In either case, assuming full thermal equilibrium, we can estimate the effective temperature rise based on the photon energy of the exciton PL peak. From the lack of spectral shifts (< 0.5 meV) of this feature in Fig. 1b in the main text, we obtain an upper bound of 5 K for the laser-induced heating at peak fluence (using the measured shift of ~0.1 meV/K in the relevant temperature range). Since the spectral shifts are assumed to be related to the phonon temperature, these observations do not exclude the possibility of initial hot carrier effects in the materials.

**d. Measurements of circular polarized components of the photoluminescence**
We measured the circular polarized emission components of the different species for
near-resonant excitation with circularly polarized light. The results are shown in Fig. 3 in
the main text and are summarized by the degree of circular polarized emission of each
species.

To obtain accurate measurements, care was needed to ensure that the pump light arriving
on the sample was circularly polarized and also that the measured components of the PL
truly corresponded to the two circularly polarized components of the light emitted from
the sample. The complications arise from wavelength-dependent depolarization effects
associated with the optical objective and the beam splitter, which deflects the emitted
radiation from the path of the incident light, as well as from the polarization sensitivity of
the CCD detector. For the case of the laser excitation, the polarization of the pump
radiation is pre-compensated with a variable wave-plate adjusted to ensure that the light
at the sample surface is precisely circularly polarized.

For detection of the photoluminescence, we made use of a Fresnel rhomb and a linear
polarizer to analyze both circular polarization states. We performed calibration
measurements using white light separately prepared in both circularly polarized states
and directed from the sample position towards the detection system. The spectra
measured for the two analyzer settings corresponding to the nominally circularly
polarized states for these defined source polarizations were used as wavelength-
dependent calibration factors.
2. Analysis of emission spectra

Our analysis of PL emission strengths of the different features in Fig. 1 of the main text is based on a careful fit of the photoluminescence spectra. Here we briefly describe the fitting procedure. We first analyzed a spectrum of moderate fluence (3 \( \mu \)J/cm\(^2\)) in terms of the six identified peaks: X, X, \( P_0 \), P\(_1\), P\(_2\), and P\(_3\). Each features was described by a Voigt line shape, the convolution of Gaussian and Lorentzian profiles. To generate spectra for different pump fluences, we then adjust the amplitudes of these components. We do not allow changes in the peak position or line shape. As shown in Fig. 1b of the main text, this produces excellent fits at all fluences.

3. Fluence dependence of emission from the different excitonic species

From the fit of the spectra described above in Sect. 2, we can extract quantitative data on the fluence dependence of the each emission features: X, X, XX, P\(_1\), P\(_2\), and P\(_3\). The results are shown in Fig. S1. We can describe the fluence dependence of the emission of these species over the measured range of fluences adequately by a simple power-law relation. The inferred exponents are \( \alpha_X = 1.20 \), \( \alpha_{X-} = 1.12 \), \( \alpha_{XX} = 1.67 \), \( \alpha_{P_1} = 0.92 \), \( \alpha_{P_2} = 0.82 \), and \( \alpha_{P_3} = 0.86 \).

We note that our analysis may underestimate the true rate of increase of the biexciton feature with fluence, since we have not allowed for any possible contribution to our measured \( P_0 \) signal from defect states near \( P_0 \). For cw excitation of heavily \( n \)-doped samples, a PL feature has been reported at an emission energy of 1.69 eV. This feature...
may contribute to the apparent strength of $P_0$ at lower fluences, thus reducing the rate of increase of the $P_0$ intensity with fluence.

In the main text, we use the data in Fig. S1a to present the fluence dependence of the XX emission in terms of the strength of the $X$ emission. The nonlinear relation between these quantities is discussed in detail in the main text. Here we briefly comment on the observed fluence dependence of the other features, i.e., of the $X, X^-, P_1, P_2,$ and $P_3$ states. The key observations are that the exciton and trion peaks exhibit slightly superlinear growth with fluence, while the defect peaks $P_1, P_2$, and $P_3$ show sublinear variation. The sublinear growth of the defect-related states is understood in terms of partial filling of the available defect sites\(^4\). The slightly superlinearly growth of the exciton and trion peaks is then be attributed to the loss of exciton and trion population to the defect states at low densities. The sublinear growth of the defect states thus induces a slightly superlinear growth of the exciton and trion populations with fluence.

4. **Exciton-biexciton coupled rate equation model**

Here we present modeling of fluence dependence of the biexciton and exciton emission features and temporal dynamics in terms of coupled rate equations, expanding on the discussion provided in the main text. Eqn. 1 in the main text is a simplified version of a more complex set of coupled rate equations that have been introduced in the literature to describe exciton and biexciton populations\(^5\). The full set of equations include terms for biexciton formation, decay, and dissociation. These coupled rate equations predict
quadratic biexciton and linear exciton density variation with laser fluence at lower
densities, but sub-quadratic behavior and sublinear behaviors at sufficiently high laser
fluence (exciton densities). The deviation at high laser fluences arises from a depletion
effect and was cited to explain the observed super-linear, but sub-quadratic behavior of
biexciton emission in prior research\textsuperscript{5,6}.

Apart from possible depletion effects, in our case, the photon energy of the laser excitation
is about 1 eV higher than that of the exciton. This suggests that hot carrier effects could
be significant. In particular, we expect that an increase in exciton kinetic energy with
pump fluence, particularly in the initial period of incomplete equilibration. The increased
exciton kinetic in turn increases the amount of energy dissipation required to form the
bound biexciton state and is expected to lead to a reduction in the biexciton formation
rate. Indeed, the role of such exciton heating effects on the formation of biexcitons has
been considered by D. Birkedal \textit{et al.}\textsuperscript{7} to explain the sub-quadratic power dependence of
the biexcitons observed in quantum wells. In this work, the authors could identify the
presence of carrier heating effects from detailed signatures in the spectroscopic widths of
different emission species.

As a simple model of this heating effect in our experiment, we assume the biexciton
formation rate $\beta$ introduced in the main text varies with exciton fluence $F$ as $\beta = \beta_0/[1 +
F/F_0]$, where the parameter $F_0$ characterizes the fluence at which the recombination
rates drops to half its low fluence value. Including this effect, we can then apply the
standard coupled rate equations in the literature\textsuperscript{5} to describe \textit{simultaneously} the fluence
dependence and the temporal dynamics observed in our measurements. (As discussed in
the main text, we expect that the biexciton thermal dissociation rate to be negligible for the low temperature measurements and have, for clarity, omitted this term from the rate equations.) The temporal evolution of exciton density $N_X$ and biexciton density $N_{XX}$ are then governed by the coupled equations:

$$\frac{dN_X}{dt} = -\gamma_X N_X + \gamma_{XX} N_{XX} - 2 \beta N_X^2$$  \hspace{1cm} (S1)

$$\frac{dN_{XX}}{dt} = -\gamma_{XX} N_{XX} + \beta N_X^2,$$  \hspace{1cm} (S2)

where $\beta = \beta_0/[1 + F/F_0]$ and $\gamma_X$ and $\gamma_{XX}$ represent, respectively, the density independent decay rates for the exciton and biexciton populations from combined radiative and non-radiative channels. The decay of the biexciton is assumed to lead to the generation of an exciton. In integrating Eqns. S1 and S2, we assume an initial exciton density given by the density of absorbed pump photons. The exciton population is taken to rise instantaneously in accord with the sub-picosecond duration of the excitation pulse.

These simple rate equations allow us to reproduce the key experimental result of the relation between the biexciton and exciton emission as a function of excitation density (Fig. S2). We are also able to model the temporal dynamics of each species (Fig. S2, inset). For a comparison of the predicted temporal dynamics with experiment, we have convoluted the results of the model with the instrument response function (IRF) for the time-resolved PL measurements.

Since the exciton and biexciton populations are coupled through Eqns. S1 and S2, their recombination dynamics are expected to exhibit dependence on the pump fluence. Fig. S3 shows that within the range of experimentally relevant pump fluences, there is,
however, essentially no predicted change in biexciton emission dynamics; the exciton emission lifetime increases slightly with increasing excitation fluence as a consequence of the biexciton decay into an exciton.

In our experimental data, there seems a weak trend for the exciton lifetime to increase at higher pump fluence (Fig. S4a). Unfortunately because of the weak biexciton PL at low fluence, we are unable to obtain a time trace of the biexciton emission time in this regime.

5. Effects of dielectric screening on biexciton binding energy

a. Effects of changing the dielectric environment of the sample

Reduced dielectric screening between charges in the sample is expected to enhance the exciton binding energy and to result in a correspondingly larger biexciton binding energy. We have examined this issue by studying the influence of the external dielectric environment on the biexciton emission feature. In particular, we have prepared a freely suspended WSe$_2$ sample for comparison with the original WSe$_2$ samples supported on oxidized silicon wafers. As shown in Fig. S5, the spectral shift between the exciton and biexciton peak implies that the exciton binding energy increases by 1.7 meV for a suspended sample compared to a sample supported on the oxide surface. Difficulties in fabrication limited our study to a single suspended sample. The reproducibility of our measurement of the biexciton binding energy, however, suggests that this relatively small observed change in binding energy is a robust quantity: from the spectral shifts of the exciton / biexciton emission features, we obtained binding energies for the three different
supported samples of 52.8 meV, 52.4 meV and 51.7 meV, with a standard deviation of just 0.6 meV. We expect no greater uncertainty in the determination of the binding energy of the suspended sample.

The observed enhancement of binding energy is thus ~4% for the suspended sample compared to a supported one. In addition to the fact that we are only changing the external medium on one side of the sample, such relatively small difference might also reflect unintentional water adsorption on samples (both supported and suspended), which would further reduce contrast of dielectric screening between the suspended and supported samples. We note that defect emission peaks in Fig. S5, unlike the biexciton peak, do not show any change in energy relative to the exciton feature, further confirming the difference in the origin of the biexciton peak.

b. Effects of changing the doping level of the sample

We have also examined the influence of carrier doping on the biexciton feature. To this end, we also prepared and characterized an electrostatically gated WSe$_2$ monolayer. When biased to achieve strong $n$-doping for comparison with ungated sample, the PL was found to be dominated by charge-related emission features (Fig. S6), as discussed by A. Jones et al.$^2$. Unintentional doping effects prevented study of the $p$-doped region.

Interpretation of these measurements is complicated by the fact that fabrication of the device induces degradation of the sample. This in turn causes strong photodoping effects under laser excitation, in addition to the pronounced defect-related emission described
above. For these reasons, we were not able to identify any spectral shift in the biexciton emission peak with doping.

The data in Fig. S6 does, however, indicate that the biexciton peak is significantly reduced in strength relative to that found in ungated samples. In particular, the dominant emission feature in the strongly doped sample is the trion feature. This result is compatible with our assignment of peak $P_0$ as the biexciton. At high doping levels, rather than initially forming neutral excitons, the sample will contain almost exclusively trions. Unlike the case for collisions of neutral excitons, we expect that for these charged entities there will be a large Coulomb barrier to the formation of biexcitons. This would lead to the formation of far fewer biexcitons, just as observed experimentally. Thus, although we are unable to observe spectral shifts of the biexciton under gating analogous to the influence of dielectric screening described above, the results of our study with respect to the biexciton emission strength also support our assignment of the biexciton feature.

6. Spectroscopic analysis of biexciton binding energy

In the main text, we define the biexciton binding energy as the difference in energy between two bright excitons and a biexciton. In addition to the bright A excitonic states (X), theory predicts the existence of different types of dark excitons\(^8\) (intra- and intervalley), which we denote generically as $X'$. These dark states may have energies similar to or few 10's of meV lower than the bright exciton states.\(^8\) Here we consider how these dark states may be involved in the formation of the observed biexciton state and how this influences
the interpretation of the biexciton binding energy in terms of spectral shifts. In addition to the formation of the observed biexciton state from two bright excitons \((X + X)\), we also consider the production of the biexcitons from a bright and a dark exciton \((X + X')\). We exclude the possibility of a biexciton produced from two dark excitons. We assume that such a state will have a low radiative rate and would not correspond to the emissive biexciton state that we observe in our PL measurements.

We now generalize our definition of binding energy \(\Delta_{XX}\) to one that reflects the difference in energy between the initial state of two excitons and the final state of a single biexciton in the two cases:

\[
E_X + E_X = E_{XX} + \Delta_{XX} \quad \text{or} \quad E_X + E_{X'} = E_{XX} + \Delta_{XX},
\]

(S3)

where \(E_X (E_{X'})\) is the energy of bright (dark) exciton, and \(E_{XX}\) is the energy of the observed biexciton state. To relate these definitions to experimentally measurable quantities, we obtain information about the energy of the biexciton by consideration of the radiative decay process. We assume that emission of a photon from the biexciton eliminates the bright exciton component. Then in the two cases above, we have

\[
E_{XX} = \hbar \omega_{XX} + E_X \quad \text{or} \quad E_{XX} = \hbar \omega_{XX} + E_{X'}.
\]

(S4)

From Eqn. S3, we then find that the binding energy is given in either case by the spectral shift between the bright exciton and biexciton emission, namely,

\[
\Delta_{XX} = E_X - \hbar \omega_{XX} = \hbar \omega_X - \hbar \omega_{XX},
\]

(S5)
where $\hbar \omega_X = E_X$ denotes the emission energy of the bright exciton state.

We note that the same argument holds if we replace the dark state with a trion. This scenario, however, appears to be unlikely, since charged biexcitons in 2D systems are predicted to be unstable when formed with electrons and holes of similar mass.\(^9\)

### 7. Thermal stability of biexcitons

In addition to the analysis of biexciton binding based on the spectral shifts given in the main text and in the previous section, we have also probed the binding of biexcitons by examination of their thermal stability through temperature-dependent PL measurements, as introduced in the main text.

The biexciton emission is rather flat for temperatures below 30 K and then decreases to a low value for temperatures above 70 K (Fig. 2c of main text). Several factors can contribute to the variation in emission strength with temperature, including changes in the radiative rate and emission time of the biexciton species. As noted above, the measured emission time did not exhibit significant dependence on temperature. The variation of the biexciton radiative rate with temperature is not as directly accessible to measurement. The observed variation in biexciton emission with temperature is, however, unlikely to originate from this effect. Indeed, within the relevant temperature range (10 K - 70 K), the measured biexciton emission line width exhibited little variation with temperature. For exciton emission, if this broadening is assumed to be homogeneous in character, then radiative rate should scale inversely with the line width, *i.e.*, should not
change significantly, for the relevant regime of the line width exceeding the thermal energy.\textsuperscript{10}

In view of these considerations, we expect that the observed variation in PL intensity with temperature is predominantly a reflection of the biexciton population. The characteristic increase and saturation in emission with decreasing temperature are compatible with full thermal equilibrium between free excitons and the biexciton species. However, the plateau in biexciton emission at low temperature would then imply a strong depletion of free excitons, which is precluded by the PL data.

We can, however, explain the observed trend in the temperature-dependent PL based on a simple model of biexciton formation in competition with thermal dissociation. Full thermal equilibrium is not achieved because of the short lifetime of the exciton and biexciton species. Since the dominant effect is the thermal activation of the dissociation process, we neglect, as a simple approximation, the temperature dependence of the biexciton formation rate. We can then model the formation of biexcitons as a function of temperature by Eqn. 1 in the main text, where we take all parameters except the biexciton decay rate $\gamma$ as temperature independent.

As introduced in main text, we write this decay rate as the sum of a temperature independent term present at low temperatures and a thermally activated dissociation term: $\gamma(T) = \tau_{XX}^{-1} + k_0 \exp(E_a/k_BT)$. Here $\tau_{XX} = 31 \text{ ps}$ is the experimentally determined biexciton lifetime at 10 K; the dissociation rate is described by an activated form in terms with prefactor $k_0$ and activation energy $E_a$ for thermal energy $k_BT$. 
The predicted biexciton PL, which is proportional to the time integral of the biexciton density $N_{XX}$ will then scale according to Eqn. 1 as $\gamma^{-1}(T)$.

In Fig. 2c we compare the predictions of this model to the experimental data for the biexciton PL as a function of temperature. An adequate fit can be obtained for a range of different activation energies and pre-factors. In particular, we can set the activation energy for thermal dissociation equal to the biexciton binding energy determined by the spectral shift, i.e., $E_a = \Delta_{XX} = 52$ meV. This fits the experimental data for a pre-factor of $k_0 = 8 \times 10^{14}$ s$^{-1}$. If choose a more intuitive value for the pre-factor of $k_0 = 1 \times 10^{13}$ s$^{-1}$, the fitting yields smaller activation energy of $E_a = 30$ meV (Fig. 2c). Some deviation between the biexciton binding energy inferred from the spectral shift and the thermal activation behavior is not unexpected. In addition to the extreme simplicity of the model, the treatment neglects the possibility of an effective biexciton temperature that exceeds the nominal sample temperature. Although both transient and cw heating of the phonons are minor under our experimental conditions (see SI Section 1), a transient increase in the electronic temperature during the picosecond lifetime of the biexcitons might still be significant. Also, the activation energy for dissociation of biexcitons into species other than two bright excitons, with lower energies, might provide a lower-barrier pathway for thermally activated decay.

8. Variational calculation of biexciton binding energy and wavefunction
We explore the biexciton state theoretically using a variational calculation within an effective mass approximation. Followings Refs\textsuperscript{11,12}, we employ a two-dimensional, four-particle Hamiltonian

\[ H_{XX} = -\frac{\hbar^2 \psi_1^2}{2m_e} - \frac{\hbar^2 \psi_2^2}{2m_e} - \frac{\hbar^2 \psi_a^2}{2m_h} - \frac{\hbar^2 \psi_b^2}{2m_h} - V(r_{1a}) - V(r_{1b}) - V(r_{2a}) - V(r_{2b}) + V(r_{12}) + V(r_{ab}). \]  

(S6)

Here \( m_e \) is the effective mass of the electrons indexed by \((1,2)\), \( m_h \) is the effective mass of the holes indexed by \((a,b)\), and \( r_{ij} = |r_i - r_j| \). The interaction potential \( V \) of the charge carriers is a distinctive aspect of this calculation. As described in the Methods section, we use a non-local screening of the Coulomb potential to describe the interaction between charged carriers within the atomically thin 2D layer. The values of the parameters in this Hamiltonian also are presented in the Methods section.

The eigenvalues and eigenfunctions of the biexciton Hamiltonian cannot be determined analytically. In our variational calculation we follow Kleinman’s\textsuperscript{13} work on biexcitons in quantum wells\textsuperscript{13} (however, note the correction in Denschlag’s work\textsuperscript{14}). In particular, we use a six-parameter variational wavefunction proposed by Brinkman, Rice, and Bell\textsuperscript{15}:

\[ \Psi([r_i]; \alpha, \beta, \nu, \rho, \lambda, \tau) = \varphi([r_i]; \alpha, \beta) \chi([r_i]; \alpha, \nu, \rho, \lambda, \tau) \]  

(S7)

with

\[ \varphi([r_i]; \alpha, \beta) = \exp[-(r_{1a} + r_{1b} + r_{2a} + r_{2b})/\alpha] \cosh[\beta(r_{1a} - r_{1b} - r_{2a} + r_{2b})/2\alpha] \]  

(S8)

and

\[ \chi([r_i]; \alpha, \nu, \rho, \lambda, \tau) = (r_{ab}/\alpha)^\nu \exp[-\rho r_{ab}/\alpha] + \lambda \exp[-\tau r_{ab}/\alpha]. \]  

(S9)
The function $\varphi$ interpolates between a biexciton complex with equal sharing of charges (at $\beta = 0$) and two completely separated excitons (at $\beta = 1$), where in both cases the exciton species have an effective Bohr radius proportional to $\alpha$. The function $\chi$ introduces important correlation between like charges. The expectation value of the Hamiltonian for a given trial wavefunction is still a challenging six-dimensional integral. By using a simplified form of the interaction potential, $V(r) = (1 - e^{-\gamma r})/\epsilon r$, much of the integration can be performed analytically in terms of Bessel functions. We have fit this simplified form to the screened interaction described in the Methods section, and confirmed that both interactions give the same neutral exciton binding energy. (Please note that the parameters $\beta$ and $\gamma$ carry different meaning, and are different quantities compared with parameters appeared in main text Eqn. 1)

The variational parameters which minimize the total biexciton energy are calculated to be $\alpha = 8 \, \text{Å}, \beta = 0.54, \nu = 1, \rho = 0.21, \lambda = 0.86, \text{and} \tau = 0.90$. These values are similar to those found by Kleinman\textsuperscript{13} for an interaction with small $\gamma$, which most closely mimics the nonlocal screening described in the Methods section. These variational parameters describe a correlated four-particle, eight-dimensional wavefunction (Eqn. S7), which is challenging to visualize. To present a physical picture of the state, we plot the total electron density of the biexciton for fixed positions of the two holes, choosing a typical separation between the holes of approximately 3.5 nm. The overall picture of the biexciton (Fig. 4 of main text) can then be seen to be that of two excitons of approximately 1 nm radius separated from one another by 3 – 4 nm.
The binding energy of the biexciton emerging from optimization of the variational parameters is 37 meV. As discussed in the main text, based on related studies in the literature for the conventional Coulomb potential, we expect that the exact solution of the model Hamiltonian would yield a binding energy 40–50% higher than this variational limit.

For the same choice of model parameters, we calculate a neutral exciton binding energy of 450 meV, which is slightly larger than the experimental value of 370 meV\textsuperscript{16}. Using our best estimate of the biexciton binding energy, which includes the correction seen in the ideal 2D limit as discussed above, the purely theoretical Haynes factor is then found to be 0.12. Our calculation has neglected additional screening mechanisms due to substrate or doping effects, which can be accounted for to provide better agreement with the neutral exciton binding energy. The Haynes factor is expected to be relatively unchanged, however, since the decrease in the exciton binding energy will be compensated by the decrease in the biexciton binding energy.
Supplementary References


Figures

**Fig. S1 | Fluence dependence of different emission features.** a, PL intensity of the excitonic (X, X' and XX) and b, defect-related (P₁, P₂ and P₃) features as function of applied laser fluence. The symbols show the experimental data and the solid lines are power-law fits, with exponents of $\alpha_X = 1.20$, $\alpha_{X'} = 1.12$, $\alpha_{XX} = 1.67$, $\alpha_{P_1} = 0.92$, $\alpha_{P_2} = 0.82$, and $\alpha_{P_3} = 0.86$. The dashed lines represent a linear dependence ($\alpha = 1$), for comparison.
Fig. S2 | Biexciton emission strength and dynamics: comparison of experimental data and the coupled-rate equation model. The main figure shows the biexciton emission plotted logarithmically against the exciton emission strength. The blue points are the experimental data and the red triangles are the results of solving the coupled rate equation model with a fluence-dependent biexciton formation rate \( \beta = \beta_0/[1 + F/F_0] \). Here \( F \) is the excitation fluence and \( F_0 = 5 \mu J/cm^2 \) is fluence at which the recombination rates drops to half its low fluence value. The model also simultaneously fits the temporal dynamics of the biexciton and exciton emission, as shown in the inset. The solid points represent the experimental data (for a fluence of \( F = 8.1 \mu J/cm^2 \)) and the solid curves are the results of the simulation with \( \beta_0 = 1.0 \text{ cm/s}, \gamma_X^{-1} = 7 \text{ ps}, \text{ and } \gamma_{XX}^{-1} = 27 \text{ ps} \).
**Fig. S3.** | **Numerical simulation of exciton and biexciton temporal dynamics from the coupled rate equations.** a, Exciton and b, biexciton dynamics after excitation with a short pulse based on Eqns. S1 and S2. The results are convoluted with our IRF for comparison with experiment. $I_{\text{dep}}$ denotes the fluence at which depletion of excitons becomes significant, with comparable exciton and biexciton populations. As the pump fluence is increased, the model predicts little change in the biexciton dynamics, but a slight increase in the exciton lifetime.

**Fig. S4.** | **Experimental results for the exciton and biexciton temporal dynamics.** a, Time-resolved exciton photoluminescence for the two indicated pump fluences and b, the biexciton dynamics at the higher pump fluence. At the lower fluence, the biexciton emission is too weak to record the dynamics. The sample temperature was 10 K.
Fig. S5 | Comparison of biexciton binding energy for suspended and supported WSe$_2$ monolayers. The black and red solid curves are, respectively, PL spectra of supported and suspended samples under pulsed laser excitation. The spectra have been shifted to match the energy of the neutral exciton emission (blue dashed line). The biexciton emission energies are marked by black (supported) and red (suspended) dashed lines. The spectral shift of biexciton emission with respect to neutral exciton emission for suspended samples exceeds that for supported samples by 1.7 meV, implying a higher biexciton binding energy for the former. The spectral shifts for emission from defect-related states are unchanged for the two cases (grey dashed lines).
Fig. S6 | PL spectra for an electrostatically gated WSe\textsubscript{2} monolayer. a, PL spectra for a low doping level and b, for heavy n-doping. For each case, emission spectra are presented for low and high excitation fluence, normalized to the same peak emission strength in each case. For the lightly doped case, an emission component (red curve) is present at the energy of the biexciton peak for high excitation fluence, which is absent at low excitation fluence. For the case of the highly doped sample, the spectrum is dominated by emission from the trion at both high and low fluence. There is only a small emission component corresponding to the biexciton (red curve).