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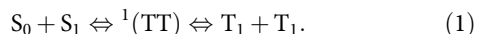
Magnetic dipolar interaction between correlated triplets created by singlet fission in tetracene crystals

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Singlet fission can potentially break the Shockley–Queisser efficiency limit in single-junction solar cells by splitting one photoexcited singlet exciton (S_1) into two triplets ($2T_1$) in organic semiconductors. A dark multiexciton state has been proposed as the intermediate connecting S_1 to $2T_1$. However, the exact nature of this multiexciton state, especially how the doubly excited triplets interact, remains elusive. Here we report a quantitative study on the magnetic dipolar interaction between singlet-fission-induced correlated triplets in tetracene crystals by monitoring quantum beats relevant to the multiexciton sublevels at room temperature. The resonances of multiexciton sublevels approached by tuning an external magnetic field are observed to be avoided, which agrees well with the theoretical predictions considering a magnetic dipolar interaction of ~ 0.008 GHz. Our work quantifies the magnetic dipolar interaction in certain organic materials and marks an important step towards understanding the underlying physics of the multiexciton state in singlet fission.

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The spin-allowed singlet fission (SF) process is highly efficient in some organic semiconductors^{1–9}. By creating two triplet excitons from a single photoexcited singlet exciton, the SF process of carrier multiplication can be implanted in multiple device architectures to improve the efficiency of solar conversion^{10–14}. However, the intrinsic mechanism responsible for the fast fission process is still under intense debate, despite remarkable progresses have recently been made^{2–8,15–22}. The essential role played by the intermediate multiexciton (ME) state (¹(TT)) has been realized^{1–5,15,17,20} with the SF process being described as¹,



The doubly excited ME state, also referred to as the correlated pair of triplet excitons, which are entangled with spin coherence, is created when a singlet-excited molecule shares its energy with a neighbouring molecule at its ground state. The magnetic interaction between the correlated triplets is insightful for revealing the nature of the ME state by providing valuable information about their spatial separation and the effect of spin coherence^{17,20,23}. However, it is challenging to quantify the weak magnetic dipolar interaction between the correlated triplet excitons at the ME state with a short lifetime^{18,20}.

Magnetic dipolar interaction is pivotal for many technically significant processes in organic materials including exciton fission/fusion¹, organic magneto-resistance²⁴ and organic photovoltaics²⁵. In a SF sensitizer, a conceivable approach to quantify the magnetic dipolar interaction is to investigate the interaction-induced energy shift of the ME state. In crystalline tetracene, the energy differences between the ME sublevels can be monitored through quantum beating signals in the singlet population^{17,20,26}. As depicted in Fig. 1a, exciton fusion from two ME sublevels induces quantum beats in population of the S_1 state, manifesting themselves as an oscillation in the time-resolved fluorescence (TRFL) spectrum. After first introduced in 1980s²⁶, this quantum beat phenomenon in tetracene has recently

been re-examined and comprehensively explained by Bardeen's group^{17,20,27}. Being a direct evidence of the ME state, the quantum beating signal has been regarded as a fingerprint of SF in tetracene^{15,17,20}. However, the signature of magnetic dipolar interaction has never been directly captured in tetracene^{20,26}, and only an upper bound of ~ 0.2 GHz was given due to the limitations in previous experiment²⁰.

Here we exploit a new scenario of the interaction-induced anti-crossing to quantify the interaction strength in crystalline tetracene. We manipulate the ME sublevels by applying an external magnetic field to approach the level-crossing resonance. The magnetic dipolar interaction between the correlated triplets causes an avoided level crossing, resulting in two branches of levels with an energy gap. The interaction strength is proportional to the gap size that can be precisely evaluated by measuring the frequencies of quantum beats relevant to the resultant upper and lower levels with TRFL spectroscopy. With this approach, we have succeeded in quantitatively determining the magnetic dipolar interaction between the correlated triplet excitons at the ME state to be ~ 0.008 GHz. The unexpected weak interaction strength indicates that it is necessary to consider the exciton size for a comprehensive understanding of the SF process.

Results

Theoretical consideration. Figure 1 schematically shows the scenario of the quantum beats relevant to the ME sublevels involving in the SF process. We describe the sublevels of ME state with a spin-dependent Hamiltonian of two correlated triplets. The Hamiltonian includes two isolated triplets (for example, α and β) and their mutual interaction (H_{int})²⁰, that is,

$$H_{\text{sp}}^{\text{TP}} = H_{\text{sp}}^{\alpha} + H_{\text{sp}}^{\beta} + H_{\text{int}}. \quad (2)$$

The isolated triplet dipole (for example, α or β , as represented by 'Tri') can be described by the Hamiltonian as^{20,28}

$$H_{\text{sp}}^{\text{Tri}} = g\mu_B \mathbf{B} \cdot \mathbf{S} + D^* (S_z^2 - S^2/3) + E^* (S_x^2 - S_y^2). \quad (3)$$

Here the first item represents the Zeeman shift due to the applied magnetic field, where \mathbf{S} , \mathbf{B} , μ_B and g are the spin operator, the external magnetic field, the Bohr magneton and the Lande g -factor, respectively. The latter two terms give zero-field Hamiltonian with parameters of D^* and E^* characterized by ESR experiments²⁹. The Hamiltonian for the magnetic dipolar interaction between the correlated triplet dipoles can be written as²⁴

$$H_{\text{int}} = X [\mathbf{S}^{\alpha} \cdot \mathbf{S}^{\beta} - 3(\mathbf{S}^{\alpha} \cdot \mathbf{R}/R_0)(\mathbf{S}^{\beta} \cdot \mathbf{R}/R_0)], \quad (4)$$

where \mathbf{S}^{α} and \mathbf{S}^{β} are the spin operators of the two triplets, \mathbf{R} is the displacement vector between the two triplets with the magnitude of R_0 and X is the parameter of interaction strength. As described in Supplementary Note 1, we calculate the energies of the ME sublevels by solving the Hamiltonian of equation (2) with a basis of nine eigenstates ($|\phi_{\text{TP}}^i\rangle$). In spite of weak magnitude, the interaction part can cause substantial differences from the energy levels predicted by the interaction-free model (Supplementary Figs 1 and 2). Those sublevels with non-zero mapping to the S_1 state ($|\langle S_1 | \phi_{\text{TP}}^i \rangle|^2 \neq 0$) involve in the exciton fission/fusion processes and directly contribute to the quantum beats (Fig. 1a)²⁰.

Theoretical calculation predicts a sublevel crossing with a magnetic field of ~ 420 G applied along the x axis (Supplementary Fig. 1). The mutual interaction opens a gap of $\Delta \approx 2X$ at the level-crossing resonance (Fig. 1c, Supplementary Fig. 1b,d). Since the gap size is small, it is difficult to directly measure the beat frequencies in time domain due to damping of the oscillations²⁰. To overcome this obstacle, we slightly tilt the external magnetic field with a small angle (θ) relative to the x axis

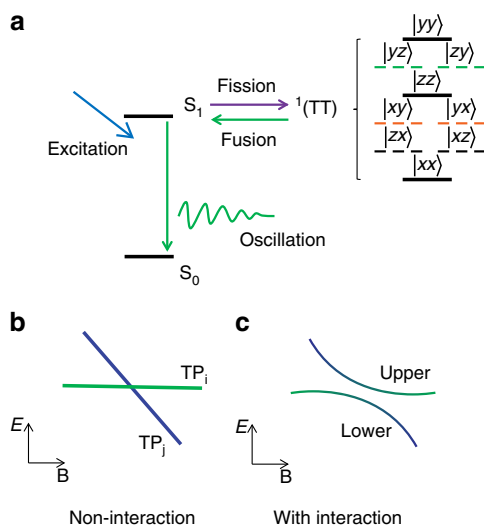


Figure 1 | Interaction-induced anti-crossing among ME sublevels.

(a) The scenario of the quantum beats related to the ME sublevels in tetracene crystals at zero field. Exciton fusion from sublevels of ME state induces the delayed fluorescence where quantum beats manifest themselves as oscillations in the TRFL spectrum. (b,c) The field dependences of two near-resonant sublevels for the cases of non-interaction and with interaction between correlated triplets, respectively. With magnetic interaction, the emergence of mixed states results in an avoided crossing with separated upper and lower branches (c).

in the xy plane (Fig. 2a) to introduce an extra perturbation (δE_y) in the Hamiltonian. The gap size then increases to be $\Delta \approx 2X + 2\delta E_y$ (Supplementary Note 2), so the evaluation becomes more accurate because the visibility of quantum beat is significantly enhanced in the TRFL trace.

Level-crossing resonance. Figure 2b plots the TRFL traces recorded under different magnetic fields at $\theta \sim 2^\circ$. An anomalous oscillation with the frequency of ~ 0.05 GHz emerges due to the newly opened gap when the field is at 420 G (inset, Fig. 2b). The field-dependent amplitudes and frequencies of the measured quantum beats (Fig. 2c) are compared with theoretical calculations (Supplementary Fig. 3) to further confirm the above assignments. The interaction-free model can well explain the observed high-frequency beats (> 0.1 GHz) (Supplementary Fig. 3), but fails to account for the anomalous part (~ 420 G) without considering the opened energy gap (Δ). A control experiment has been performed with the magnetic field applied at z direction (Supplementary Note 3). Under this configuration, the anomalous beat no longer exists since no level crossing is found (Supplementary Figs 6 and 7), verifying that the observed low-frequency quantum beat is indeed a result of gap opened by the magnetic dipolar interaction and perturbation.

Next, we analyse the θ -dependent oscillatory components to quantify the interaction strength (Fig. 3a). We assume the displacement vector (\mathbf{R}/R_0) to be along the nearest neighbour orientation^{3,16}. The resonant energies of all nine ME sublevels are calculated by exactly diagonalizing Hamiltonian (2) and indexed by their zero-field energies. When the magnetic dipolar interaction is included (Supplementary Fig. 1), the avoided crossing occurs between the three and four sublevels (Fig. 3c) as well as the sixth, seventh and ninth sublevels (Fig. 3d) at ~ 420 G.

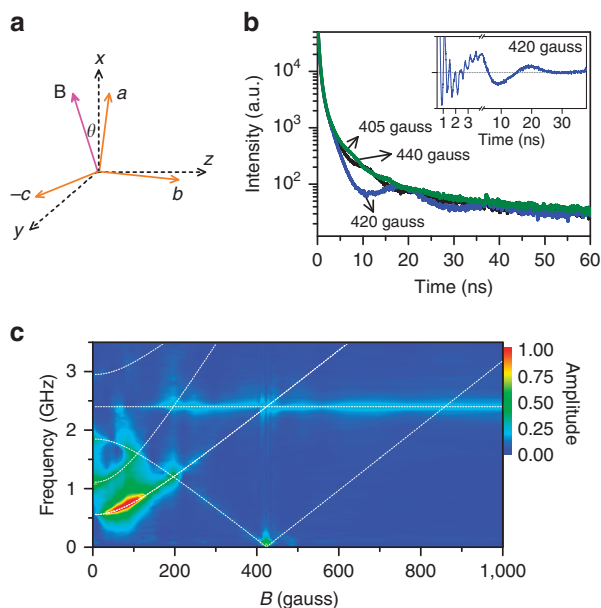


Figure 2 | Magnetic-field-dependent quantum beats. (a) Schematic diagram of the external magnetic field applied at the xy plane with a small angle (θ) tilted relative to the x axis. (b) The decay curves of fluorescence dynamics with three different external magnetic field value tilted at $\theta = 2^\circ$ near the resonance of level crossing. Inset shows the oscillation part obtained by subtracting the multi-exponential decay components from the raw data recorded at 420 G. (c) The relative amplitudes of quantum beats are plotted as functions of the beat frequency and the field magnitude. The dashed lines indicate the expected beat frequencies calculated with interaction-free model.

The mapping products of $|\langle S_1 | \phi_{TP}^i \rangle|^2$ for selected sublevel pairs, which directly reflect the beating amplitudes, are compared in Fig. 3e,f, suggesting the dominant contribution from the third and fourth sublevels (Supplementary Note 2; Supplementary Fig. 5). In Fig. 3b, the measured peak oscillation frequency of this anomalous beating signal as a function of the tilt angle θ is compared with the theoretical curves of energy separation between three and four sublevels calculated with different interaction strengths. The perturbation induced by field tilting corresponds to the zero-interaction curve ($X = 0$) in Fig. 3b with $\delta E_y \propto \theta$ (Supplementary Fig. 4). The disparity of experimental data from the linear dependence on the tilt angle near $\theta \approx 0$ is an evidence of existing magnetic dipolar interaction, which can be best reproduced by calculation with the interaction strength of $X = 0.008$ GHz (Fig. 3b).

Strong magnetic field limit. Furthermore, we have also examined the quantum beats at the strong magnetic field limit. A field of $\sim 3,000$ G is applied in the xz plane with an angle of Φ to the x axis as shown in Fig. 4a. In this regime, multiple beat frequencies collapse into one frequency, because only two sublevels dominate the mappings to the S_1 state (Supplementary Fig. 2; Supplementary Note 4)²⁷. The energy alignments of the two sublevels calculated using models with and without the interaction are shown in Fig. 4c,b, respectively. The two sublevels approach to degeneracy at $\Phi \approx 69^\circ$ (Fig. 4b), which is avoided due to the magnetic dipolar interaction (Fig. 4c). The oscillatory amplitude is plotted as a function of delay time and the angle deviated from the degeneracy value ($\Delta\Phi$) in Fig. 4d. The measured $\Delta\Phi$ -dependent beat frequencies shown in Fig. 4e agree well with the calculated curve having $X = 0.008$ GHz. The value agrees well with that obtained at 420 G, which is significantly larger than the bounds of errors and spurious effects including the hyperfine coupling as discussed in Supplementary Methods (Supplementary Table 3). The strength measured here is at the same order of magnitude as that adopted to interpret the data of optically detected magnetic resonance of germinate triplet pair at the $T_1 + T_1$ state in bis(triisopropylsilyl)ethynyl-tetracene films²³. The weak magnitude measured here is also in consistency with the upper bound estimated in literature²⁰ and theoretical analysis of other magnetic effects³⁰. It is over two orders of magnitude smaller than the energy difference between the sublevels at zero field, which might explain why the signature of this magnetic dipolar interaction was absent in previous studies^{20,26}.

Discussion

The orientation of displacement vector (\mathbf{R}/R_0) with respect to the z axis of magnetic tensor may affect the evaluation of the interaction strength. We have considered all four possible configurations for two neighbouring molecules in ab plane (Supplementary Fig. 8). The interaction strength X that best reproduces the experimental data (Figs 3f and 4d) is far below the theoretical values for two nearest neighbour molecules (Supplementary Tables 1 and 2). The separation distance between two triplets at the ME state equivalent to the measured value of X can be estimated to be ~ 1.7 nm, which is about two to four times of the intermolecular distance (Supplementary Note 5). The unexpected large separation between the correlated triplets can be plausibly caused by the delocalization effect of photoexcited singlet excitons³¹. Previous PL study has suggested the size of singlet excitons to be in the order of tens of molecules at low temperature³¹, which might also affect the exciton dynamics in certain extent at room temperature⁷. The pair of triplets resulted from the delocalized singlet excitons can distribute over

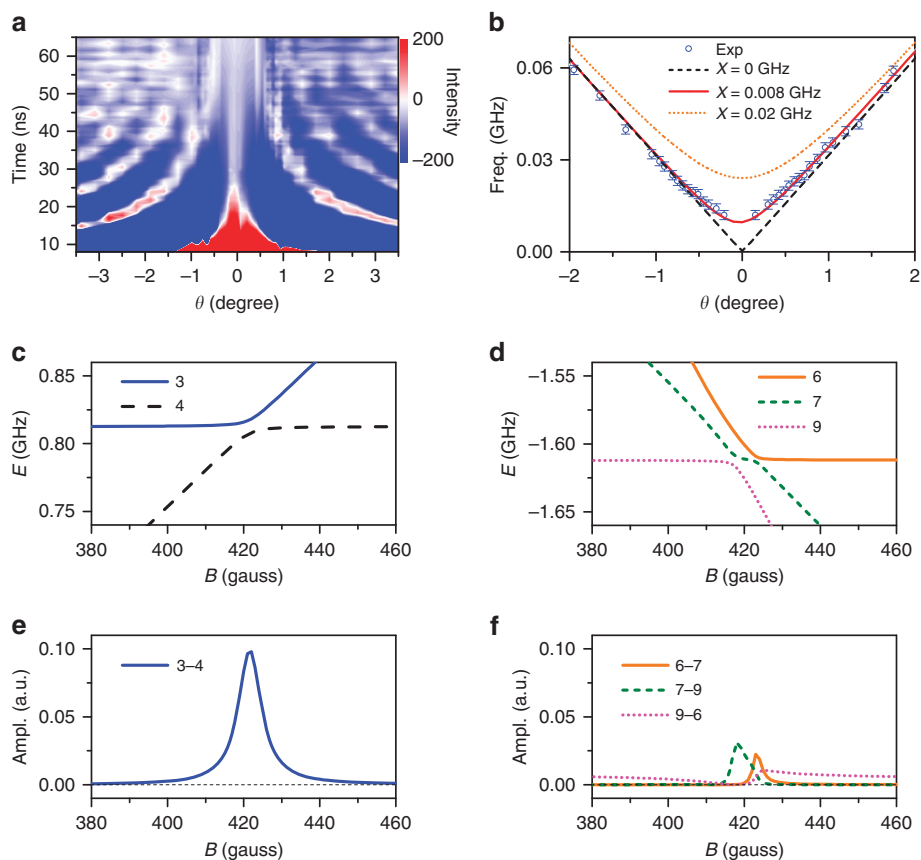


Figure 3 | Quantum beats near level-crossing resonances. (a) The oscillation components are plotted versus the delay time and tilt angle (θ). The external field is set at 420 G. (b) Experimental results of θ -dependent beat frequencies are compared with theoretical calculated curves considering different strengths (X) of magnetic dipolar interaction. (c–f) Theoretical considerations of the interaction-induced anti-crossing of various ME sublevels (for details, see Supplementary Note 1). At the resonance field of ~ 420 G, the anti-crossing occurs in two cases, resulting in the mixed states of three and four sublevels (c) and the mixed states of sixth, seventh, and ninth sublevels (d). The field-dependent amplitudes of low-frequency quantum beats calculated approximately as the mapping products of selected sublevel pairs for these two cases are plotted in e and f, respectively.

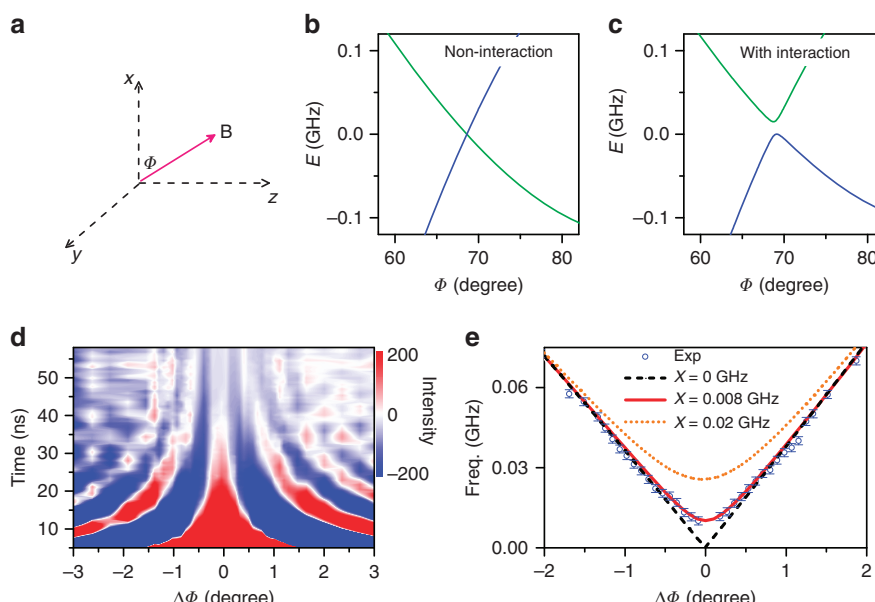


Figure 4 | Quantum beats at the strong magnetic field limit. (a) Schematic diagram of a strong field applied at the xz plane having an angle Φ with respect to the x axis. In this strong field limit, only two dominant sublevels are involved in the fission and fusion processes. (b,c) The calculated energy alignments of two sublevels for the cases of non-interaction and with interaction between correlated triplets, respectively. The level crossing occurs at $\Phi \approx 69^\circ$. (d) The oscillation components are plotted versus the delay time and the angle ($\Delta\Phi$) deviated from the resonant value. The magnitude of the external field is $\sim 3,000$ G. (e) The experimentally measured beating frequencies are plotted as a function of $\Delta\Phi$ under the strong field limit. The curves are theoretically calculated results with different strengths of magnetic interaction.

a distance of multiple molecules, which can naturally explain the measured weak magnetic interaction.

Moreover, though the diffusion of triplet excitons at the ME state remains poorly understood, triplet diffusion at the $T_1 + T_1$ state has been shown to be quite efficient in tetracene crystals³². In principle, the triplet diffusion may increase the separation distance between the triplet excitons over time and cause a time-dependent X. Such effect has not been clearly seen in this study, which could be ascribed as the consequence of quantum beat spectroscopy used in this study. As depicted in Fig. 1a, only the correlated triplet pairs that recombine through the exciton fusion process contribute significantly to the beating signal. The triplet pairs that diffuse apart may lose the spin coherence and/or the coherence needed for exciton fusion. Those triplet pairs generate delayed fluorescence but do not make significant contribution to the beating signal. Consequently, the time dependence of interaction strength is not manifested in the quantum beat spectroscopy here. Additional work will be needed to fully uncover the effect of exciton diffusion on the interaction between the triplet excitons at the ME state.

Overall, the spins of correlated triplets are weakly coupled with the environment, making our method reliable in evaluating the magnetic dipolar interaction at room temperature. This work represents the first successful quantification of the magnetic dipolar interaction between the correlated triplet excitons at the ME state in crystalline tetracene. The weak interaction strength observed here provides a direct evidence that the initial step ($S_0 + S_1 \rightleftharpoons {}^1(TT)$) of SF process involves molecules that are not nearest to each other. The entangled triplets at the ME state delocalized over many molecules arising from the delocalization of initial singlet excitons could be a plausible origin of the weak interaction strength. Such phenomena indicate that an alternative scenario different from the available models considering two proximately coupled molecules may be necessary to fully understand the SF process in crystalline tetracene. Including the effect of exciton delocalization to elucidate SF may be enlightening to address the debates between a charge-transfer mechanism and coherent superposition model responsible for the generation of intermediate ME states^{2,16,19,20,33–35}. The quantum beating behaviour in crystalline tetracene due to spin coherence of the correlated triplet pairs is sensitive to the magnitude and direction of the magnetic field. These features deserve more in-depth investigations and can stimulate further adventures in applying SF to many new areas of research such as spintronics and quantum information science^{36–38}.

Methods

Sample preparation and magnetic field alignment. Tetracene single crystals with the thickness of $\sim 1 \mu\text{m}$ and size up to $5 \times 5 \text{mm}^2$ were prepared by the method of physical vapour deposition. The crystallographic axes were determined by X-ray diffraction and polarization microscopy (Supplementary Fig. 9), which were further employed to determine the magnetic axes with a transform matrix as established by electron spin resonance measurements (Supplementary Methods). A rotatable magnetic coil was used for magnetic-field-dependent experiments. The samples were mounted on a multi-axis platform to realize the desired alignment with respect to the magnetic field.

Optical characterizations. The second harmonic field (400 nm) of the pulses emitted from a Ti:Sapphire oscillator (800 nm, Vitara, Coherent) was chosen as the excitation source. The repetition rate was reduced down to 4 MHz by a pulse picker and the excitation flux was kept at a low level ($\sim 4 \text{nJ cm}^{-2}$) to avoid the effect of exciton–exciton annihilation. The emission light was collected by a fibre and routed to a spectrograph. The TRFL spectra at 530 nm were recorded with the technique of time-correlated single-photon counting by an avalanche photodiode having a temporal resolution of better than 50 ps. The multi-exponential decay components were subtracted from TRFL traces before Fourier transform to extract the frequencies and amplitudes of quantum beating signals (Supplementary Fig. 10).

Theoretical simulation. The resonant energies of ME sublevels are calculated by exact diagonalization of the full spin-dependent Hamiltonian. Quantum beat in the detected TRFL signal is modelled by the dynamics of the density matrix elements governed by the quantum Liouville equations (Supplementary Note 1).

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Author contributions

C.Z. and M.X. conceived and designed the experiments. R.W., B.Z. and Y.L. performed the experiments. R.W. and C.Z. analysed the data. R.W., C.Z., X.W. and M.X. co-wrote the manuscript.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

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