Room-temperature coherent optical manipulation of hole spins in solution-grown perovskite quantum dots

Coherent control of spins in solid-state systems holds great promise for quantum information science. Compared with bulk semiconductor materials, localized systems (such as epitaxial-grown quantum dots (QDs)) were considered to be more adaptable to quantum information science because of the possibility of addressing and manipulating single spins. Other examples of localized systems include defect centres or dopants in solids. Traditionally, radiofrequency electrical or magnetic stimuli are implemented for spin quantum-state control, but the time limits of such operations are on the order of nanoseconds at best. Femtosecond or picosecond optical pulses have recently enabled ultrafast spin manipulation at exceptionally high speeds.

In spite of the success of various manipulation methods, there are still many shortcomings associated with current spin-host materials from the viewpoint of practical applications. Epitaxial QDs are fabricated using expensive, high-temperature and high-vacuum apparatus. Another fundamental issue is that interlevel scattering and coupling to phonon baths can strongly damp the spin coherence. Consequently, spin manipulation of these QDs is typically accomplished at cryogenic temperatures of a few kelvin. By contrast, the defect or dopant spins in solids are highly isolated and can be manipulated at room temperature. However, scaled-up production of these point defects might eventually become a challenge. For the scalable and sustainable implementation of spin-based quantum information science, it is desirable to develop low-cost materials whose spins can be coherently manipulated under ambient conditions.

The colloidal counterparts of QDs (also called nanocrystals) can be synthesized in large quantities in solution at low cost, yet with high precision in terms of size and shape control, and are particularly suitable for self-assembly or device integration. However, spin manipulation for prototypical CdSe-based colloidal QDs has not been realized at room temperature. We turn our focus to recently developed lead halide perovskite colloidal QDs. Their spin–orbit coupling and electronic structure have proved to be ideal for efficient spin injection by optical means, and their strong light–matter interaction should also facilitate spin manipulation based on an optical Stark effect (OSE). The challenge of spin manipulation in lead halide perovskite QDs, however, is their rapid spin relaxation.

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Xuyang Lin1,2, Yaoyao Han1,2, Jingyi Zhu1 & Kaifeng Wu1,2

Manipulation of solid-state spin coherence is an important paradigm for quantum information processing. Current systems either operate at very low temperatures or are difficult to scale up. Developing low-cost, scalable materials whose spins can be coherently manipulated at room temperature is thus highly attractive for a sustainable future of quantum information science. Here we report ambient-condition all-optical initialization, manipulation and readout of hole spins in an ensemble of solution-grown CsPbBr3 perovskite quantum dots with a single hole in each dot. The hole spins are initialized by sub-picosecond electron scavenging following circularly polarized femtosecond-pulse excitation. A transverse magnetic field induces spin precession, and a second off-resonance femtosecond-pulse coherently rotates hole spins via strong light–matter interaction. These operations accomplish near-complete quantum-state control, with a coherent rotation angle close to the π radian, of hole spins at room temperature.
temperature. CsPbBr$_3$ QDs of controllable sizes were synthesized using a hot-injection method$^{24}$; details can be found in the Methods. Figure 1a shows the absorption spectra of two QD samples (QD1 and QD2) dispersed in hexane. Their transmission electron microscope (TEM) images in Supplementary Fig. 1 reveal monodisperse cube-shaped dots with average edge lengths of ~4.2 and 4.6 nm for QD1 and QD2, respectively. The uniform quantum confinement results in a series of exciton peaks identifiable at room temperature, with the lowest peaks at 470 and 481 nm for QD1 and QD2, respectively (Fig. 1a). Confinement-induced energy quantization in these QDs should help to suppress phonon-induced interlevel scattering and sustain spin coherence compared with bulk samples, although their large single-dot linewidth ($\sim$50–100 meV; refs. $^{31,32}$) compared with phonon energies suggests that intralevel scattering still poses an issue at room temperature.

A carboxylated derivative of AQ, which is a well-known electron acceptor$^{33,34}$, was anchored onto the QD surface through the carboxyl group (Methods). The enhanced absorption of QD1–AQ and QD2–AQ compared with bare QD1 and QD2 in the ultraviolet can be attributed to the AQ molecules (Supplementary Fig. 2). On the basis of absorption relaxation at room temperature (a few picoseconds)$^{34,35}$, probably limited by enhanced electron–hole exchange in these confined systems$^{36}$.

In this Article, we combine interfacial charge-transfer chemistry of lead halide perovskite QDs and femtosecond laser pulses to initialize, manipulate and read out hole spins at room temperature. We functionalize the surfaces of CsPbBr$_3$ QDs with anthraquinone (AQ) molecules. Following the preparation of a spin-polarized exciton in a QD using a circularly polarized photon, the AQ can extract the electron on a sub-picosecond timescale, thus quenching the spin relaxation induced by electron–hole exchange. This results in long-lived hole spin precession about an applied transverse magnetic field up to hundreds of picoseconds, during which a second off-resonance laser pulse coherently rotates the hole spin around a longitudinal axis through the OSE. Taken together, the precession and rotation accomplish successful quantum-state control of hole spins at room temperature.

**Sample characterization and experimental set-up**

Figure 1 illustrates the sample characteristics, optical set-up and principle of our experiment. All measurements were performed at room temperature. CsPbBr$_3$ QDs of controllable sizes were synthesized using a hot-injection method$^{34}$; details can be found in the Methods. Figure 1a shows the absorption spectra of two QD samples (QD1 and QD2) dispersed in hexane. Their transmission electron microscope (TEM) images in Supplementary Fig. 1 reveal monodisperse cube-shaped dots with average edge lengths of ~4.2 and 4.6 nm for QD1 and QD2, respectively. The uniform quantum confinement results in a series of exciton peaks identifiable at room temperature, with the lowest peaks at 470 and 481 nm for QD1 and QD2, respectively (Fig. 1a). Confinement-induced energy quantization in these QDs should help to suppress phonon-induced interlevel scattering and sustain spin coherence compared with bulk samples, although their large single-dot linewidth (~50–100 meV; refs. $^{31,32}$) compared with phonon energies suggests that intralevel scattering still poses an issue at room temperature.

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spectra and extinction coefficients, we estimate that there are more than 200 AQ molecules on each QD.

An approximate energy-level diagram (Supplementary Fig. 2) of CsPbBr3 QDs34 and AQ33 predicts that electron transfer from photoexcited QDs to AQ is the only allowed charge/energy transfer pathway in the system. Electron transfer results in nearly quantitative quenching of the emissions of both QD1 and QD2 (Supplementary Fig. 2). Full characterization of the charge-transfer processes is provided in Supplementary Figs. 3 and 4; the most important conclusion is that electron transfer occurs mostly within 300 fs and the resulting QD−AQ charge-separated states live much longer than 10 ns. The extremely rapid electron transfer is mainly due to large amounts of AQ acceptors available to each QD, statistically enhancing the electron transfer rate by two orders of magnitude44. The remaining hole could have long-lived spin polarization as these halide perovskites feature an inverted band structure compared with traditional semiconductors, with weak spin–orbit coupling in their valence band27.

The band-edge optical selection rules in CsPbBr3 QDs are depicted in Fig. 1b in a quasicrystal representation33,37. In a cubic symmetry, the valence band states (s = 1/2, ms = ±1/2) are coupled to the conduction-band spin–orbit split-off states (j = 1/2, ms = ±1/2) through circularly polarized photons (σ’ and σ”, respectively). Anisotropic exchange interactions due to QD shape anisotropy or lattice distortion may diagonalize the circularly polarized excitons into linearly polarized ones34–36. But the spin-selective OSE that we will show below indicates that the spin selection rules still largely hold for the samples studied here, at least at room temperature. Moreover, our primary focus here is single-hole states, for which exchange-induced splitting is eliminated. For the same reason, random orientation of the QDs in an ensemble should not complicate data interpretation34,35, provided that the rotational motion of these nanostructures in solution takes much longer (nanoseconds36) than the spin relaxation studied here.

In the optical experiment (Fig. 1c; detailed in the Methods), we used a femtosecond laser amplifier to pump an optical parametric amplifier to generate a tunable pump pulse. Another part of the fundamental beam was frequency-doubled to generate the rotation (tipping) pulse at 151 nm. The spectra of the pump pulses for QD1 and QD2 are depicted in Fig. 1a, which are in resonance with their respective lowest-exciton peaks, whereas the tipping pulse is below their optical gaps and hence functions as off-resonance rotation. The white-light fundamental beam was frequency-doubled to generate the rotation (tipping) pulse (that is, the ΔA method in which the pump photon eliminates one of the pre-doped spins by promoting them to trion states and leaves the other type spins by promoting them to trion states and leaves the other type spin dephasing); see Supplementary Fig. 8.

Figure 2e presents the hole spin precession kinetics in QD1–AQ obtained by taking the difference between co- and counter-ΔA (that is, the ΔA method in which the pump photon eliminates one of the pre-doped spins by promoting them to trion states and leaves the other type spin dephasing); see Supplementary Fig. 8.

The zero-field kinetics of QD1–AQ are also plotted in Fig. 2e for comparison, which shows a relaxation time of 40.7 ps. By contrast, the zero-field kinetics of neutral QDs (not functionalized with AQ) of such sizes had a spin relaxation/dephasing time of only -1 ps (Supplementary Fig. 9 and Supplementary Table 2). The marked contrast between functionalized and unfunctionalized QDs substantiates that the electron–hole exchange is the limiting factor for the exciton spin lifetime and that by removing the electron long-lived hole spin coherence is attainable at room temperature. Furthermore, the exchange interaction between the hole and AQ radical anion should have a minor impact, given a very weak QD-size dependence of the hole spin lifetime (Supplementary Fig. 10). A thorough investigation of the hole spin relaxation mechanisms is beyond the scope of the current study and will be pursued in our future work.

Room-temperature hole spin precession
We first investigated hole spin injection and precession with the pump pulse on and the tipping pulse off (Fig. 1d). The pump power was controlled to be low, resulting in the average exciton number per QD ⟨N⟩ = 0.025 and 0.08 for QD1 and QD2, respectively (see Methods), and thereby removing complications from multie exciton Auger recombination44. The circularly polarized pump pulse triggers sub-picosecond electron transfer and leaves behind a spin-polarized hole. In the presence of the transverse magnetic field, the hole is in a superposition of eigenstates |↑⟩ and |↓⟩ quantized by the field: (|↑⟩ ± |↓⟩)/√2 (Fig. 2a), situated at the x axis of the Bloch sphere whose z axis is aligned with B0 (Fig. 2b). Owing to the field-induced Zeeman splitting (ΔE) of |↑⟩ and |↓⟩, the coherent state is rotated on the equator plane with the angular frequency of ω = ΔE/ℏ (that is, the Larmor precession frequency). This precession can be directly visualized by a circularly polarized probe pulse: see Fig. 2c for QD1–AQ and Supplementary Fig. 5 for QD2–AQ. As anticipated, the time-dependent ΔA spectra detected with co- and counter-polarized pump/probe configurations have exactly anticorrelated phases (compare the left and right panels of Fig. 2c).

Our spin initialization method can be viewed as an active initialization as the hole is generated by dissociating the spin-polarized exciton injected by a pump photon, that is, it carries the spin directly imprinted by the photon. By contrast, spin initialization of charge-doped QDs extensively adopted in previous studies11–15 is more like a passive method in which the pump photon eliminates one of the pre-doped spins by promoting them to trion states and leaves the other type spin in a polarized state. Although both methods work well, our method does not require pre-doped samples and its interpretation is more straightforward. It resembles, but is greatly simplified from, the electric field-induced exciton ionization method reported for epitaxial QDs14,20.

In the optical experiment (Fig. 1c; detailed in the Methods), we used a femtosecond laser amplifier to pump an optical parametric amplifier to generate a tunable pump pulse. Another part of the fundamental beam was frequency-doubled to generate the rotation (tipping) pulse at 151 nm. The spectra of the pump pulses for QD1 and QD2 are depicted in Fig. 1a, which are in resonance with their respective lowest-exciton peaks, whereas the tipping pulse is below their optical gaps and hence functions as off-resonance rotation. The white-light fundamental beam was frequency-doubled to generate the rotation (tipping) pulse (that is, the ΔA method in which the pump photon eliminates one of the pre-doped spins by promoting them to trion states and leaves the other type spin dephasing); see Supplementary Fig. 8.

Figure 2e presents the hole spin precession kinetics in QD1–AQ obtained by taking the difference between co- and counter-ΔA (that is, the ΔA method in which the pump photon eliminates one of the pre-doped spins by promoting them to trion states and leaves the other type spin dephasing); see Supplementary Fig. 8. The Landé g factor of the hole is derived as |g| = ℏω/hμB = 1.73, which is larger than the reported value for bulk-like CsPbBr3 (refs. 18,44) likely because quantum confinement modifies the g factor or because it is influenced by the surface-appended AQ. As Landé g factors should be slightly different for each QD, dephasing occurs in the course of spin precession, which becomes more obvious under stronger B0 (that is, the Δg mechanism for spin dephasing); see Supplementary Fig. 8.

The zero-field kinetics of QD1–AQ are also plotted in Fig. 2e for comparison, which shows a relaxation time of 40.7 ps. By contrast, the zero-field kinetics of neutral QDs (not functionalized with AQ) of such sizes had a spin relaxation/dephasing time of only 1 ps (Supplementary Fig. 9 and Supplementary Table 2). The marked contrast between functionalized and unfunctionalized QDs substantiates that the electron–hole exchange is the limiting factor for the exciton spin lifetime and that by removing the electron long-lived hole spin coherence is attainable at room temperature. Furthermore, the exchange interaction between the hole and AQ radical anion should have a minor impact, given a very weak QD-size dependence of the hole spin lifetime (Supplementary Fig. 10). A thorough investigation of the hole spin relaxation mechanisms is beyond the scope of the current study and will be pursued in our future work.

We note that previous time-resolved Faraday rotation measurements have observed long-lived spin precession of resident carriers in nominally neutral QDs14, probably resulting from unintentional photocharging. However, the extent of photocharging should depend sensitively on the excitation laser power. In our experiments with minimized pump powers (see above), photocharging should be negligible. Otherwise, we would expect a long-lived component of ~40 ps on the spin relaxation kinetic traces of untreated QDs, which is not seen in Supplementary Fig. 9.
Ultrasound rotation using OSE

We then studied the spin-selective OSE as a tool for coherent spin manipulation, in an experimental configuration with the pump pulse and Bz off and the tipping pulse on (Fig. 1d). This measured the OSE of neutral exciton states instead of single-hole states in the sample, but it served as a good starting point to illustrate coherent manipulation\textsuperscript{47,48}. As shown in Fig. 3a, when the system was coherently driven by, for example, a ω' tipping photon, under a quasiparticle representation, the Floquet states hybridized with only |−1/2⟩\textsubscript{h} and |+1/2⟩\textsubscript{h} states but not the other two states coupled to σ. As a result, a blueshift of the transition can be detected with a σ' photon, but not a σ' photon.

Indeed, we observed a lobe-shaped ΔA spectrum for QD1 with co-circularly polarized tipping-probe beams, which is almost absent when the beams have counter-circular polarizations (Fig. 3b); see Supplementary Fig. 11 for representative spectra of QD2. The signal is present only during tipping-probe cross-correlation time. These are consistent with spin-selective, circularly polarized OSE. By contrast, OSE measurements using linearly polarized laser beams of co- and cross-polarizations generate almost identical signal sizes, which are consistent with spin-selective, circularly polarized OSE (Supplementary Text 2). A possible reason is that at room temperature the anisotropic exchange splitting in these perovskite QDs (<1 meV)\textsuperscript{31,32} is orders of magnitude weaker than their homogeneous exciton linewidth (~50–100 meV)\textsuperscript{31,32}, thus allowing us to ignore the effect of symmetry breaking in our experiments\textsuperscript{34}.

The lobe-shaped ΔA spectral intensity increases with the tipping power $P_{\text{tip}}$ (Fig. 3c), which can be quantified as OSE-induced splitting (Δ\textsubscript{OSE}) between the |σ'⟩ and |σ⟩ excitons. The splitting grows approximately linearly with $P_{\text{tip}}$ and reaches 9.65 meV at 9.72 GW cm\textsuperscript{-2} (Fig. 3d). From the linear slope, we derived transition dipoles (μ) of 21 and 24 D for QD1 and QD2, respectively; see Supplementary Text 2 for the calculation details\textsuperscript{27}. The large μ is indicative of intrinsically strong light–matter interaction for CsPbBr\textsubscript{3} QDs, in contrast to a previous study on CdSe-based colloidal QDs that relied on a resonant plasmon enhancement effect to achieve sizable δ\textsubscript{OSE} (ref.\textsuperscript{10}).

The strong light–matter interaction of CsPbBr\textsubscript{3} QDs should facilitate coherent spin manipulation using the OSE. To illustrate this, we can interpret the OSE that lifts the degeneracy of |σ'⟩ and |σ⟩ excitons as an effective pseudo-magnetic field (B\textsubscript{eff})\textsuperscript{27,41,46,47}.
Room-temperature coherent hole spin manipulation

With the tools of spin precession and manipulation at hand, we explored complete quantum-state control of hole spins in QD1–AQ with both the pump (chopped) and tipping (un-chopped) pulses, as well as B_{tip} on (Fig. 1d). The pump powers were identical to those used in spin precession measurements, ensuring excitation in the single-exciton regime. The pump-tipping delay (t_{tip}) is controlled to investigate the tipping effects at various positions on the Bloch sphere (z axis aligned with B_{tip}). Figure 4a (top) is the spin precession kinetics tipped at $E_{tip}$ = 17.2 ps, that is, when the state is $(|+\rangle + |\downarrow\rangle)/\sqrt{2}$ on the y axis of the Bloch sphere, with a tipping power of 9.72 GW cm$^{-2}$. A large amplitude change and sign-switch from the untipped kinetics is achieved; see the corresponding Bloch sphere representation in Fig. 4b. The difference in tipping with $\sigma^+$ or $\sigma^-$ pulses is negligible (Supplementary Fig. 14). By contrast, when the tipping acts at $E_{tip}$ = 31.7 ps ($(|+\rangle - |\downarrow\rangle)/\sqrt{2}$; x axis) with the same power, a negligible amplitude change is observed (Fig. 4a, middle). Overall, tipping the states at the y axis and x axis represents the most and least obvious spin manipulations, respectively. Figure 4a (bottom) presents an intermediate case with the tipping acting at $\omega t + \phi$ = 4.4 rad between the y axis and x axis. Similar results for QD2–AQ are presented in Supplementary Fig. 15. All the tipped kinetics can be well fitted using Bloch sphere analysis; see Supplementary Text 4 and Supplementary Tables 3–6 for details.

We examined the tipping power ($P_{tip}$) dependence with $E_{tip}$ fixed at 17.2 ps (Fig. 4c), that is, tipping at the y axis. The tipping angle was calculated as $\theta_{tip} = \arccos(A_y/A_{tot})$, where $A_y$ and $A_{tot}$ are the tipped and untipped signal amplitudes, respectively. As presented in Fig. 4d, $\theta_{tip}$ of QD1–AQ increased sublinearly with $P_{tip}$ ($\theta_{tip} = P_{tip}^{0.638}$) until it reached $-2n/3$ rad at -10 GW cm$^{-2}$. The maximum $\theta_{tip}$ was solely limited by the laser power in our set-up as no sign of sample damage was observed at the largest $P_{tip}$. For QD2–AQ with a larger transition dipole and a smaller tipping detuning, $\theta_{tip}$ also increased with $P_{tip}$ sublinearly ($= P_{tip}^{0.638}$), but more steeply than QD1–AQ, reaching $0.56\pi$ rad at 3.58 GW cm$^{-2}$. A further increase of $P_{tip}$, however, resulted in real excitation of trion states because the absorption onset of QD2 was closer to the tipping pulse than QD1 (Fig. 1a). We expect that $\pi$-rad tipping (that is, full quantum-state control) should be achievable for both QD1–AQ and QD2–AQ by tailoring the tipping photon energy and bandwidth, as well as by increasing the tipping power.

The sublinear scaling of $\theta_{tip}$ with $P_{tip}$ observed herein contradicts the simple assumption of $B_{tip}$ scaling linearly with $P_{tip}$ made previously, but it is similar to a previous study on epitaxial QDs. As explained in ref. 15, when the Rabi energy ($\hbar\Omega_{tip}$) of the interaction between the electric field of the tipping pulse and the QD transition dipole becomes comparable to the detuning energy ($\Delta$), the so-called adiabatic elimination approximation breaks down and the excitation of virtual populations must be considered. For example, at $P_{tip}$ of 9.72 GW cm$^{-2}$, $\hbar\Omega_{tip}$ for QD1–AQ has reached 67.3 meV, which is indeed comparable with $\Delta = 230$ meV in our experiment. A four-level master-equation simulation in ref. 15 produced $\theta_{tip} = P_{tip}^{0.45}$, which is strikingly close to our experimental results. 

Conclusions

The complete set of initialization, manipulation and readout of hole spins in an ensemble of CsPbBr$_3$ perovskite QDs achieved here at room temperature is a very promising result. It establishes the feasibility of quantum information processing using low-cost, solution-grown samples under ambient conditions. Moreover, we found that the strategy of surface modification with charge acceptors could represent a general method to initialize long-lived carrier spins in...
perovskite QDs. As shown in Supplementary Fig. 16, by anchoring pyrene molecules onto the surfaces of CsPbCl₃ perovskite QDs to scavenge photogenerated holes, we observed electron spin precession beyond 100 ps. Further prolonging these room-temperature spin coherence times to nanoseconds, thus enabling 10⁴–10⁵ operations (for quantum error correction) using femtosecond pulses, is the next step in the roadmap.

**Online content**

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41565-022-01279-x.

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notch filter with a centre wavelength of 514 ± 2 nm and full-width at
half-maximum 230 fs were used to remove residual QD precursors in the sample.

The 1,030 nm output laser was split into two beams with an 80/20 ratio. The 80% part was attenuated with a neutral-density filter wheel. The laser delay between the pump and probe pulses was controlled by a motorized delay line and the delay between the pump and tipping pulses was controlled by a homemade delay line. The pump or tipping beam was chopped by a synchronized chopper at 5 kHz and the absorbance change was calculated with adjacent probe pulses. The probe, pump and tipping beams were focused and spatially overlapped on the sample with spot sizes of 240 μm, 270 μm and 355 μm, respectively (at 1/e² intensity), with the spot sizes measured using the knife-edge method. The pulse durations were ~540 fs at 1/e² intensity. Circular polarizations of the pump, tipping and probe beams were controlled by quarter waveplates. The magnetic field direction was perpendicular to the laser beams, and provided by an electromagnet (EM3; Beijing Jinzhengmao Technology Co.).

Using the pump beam size, the pump power and photon energy, we calculated that in our experiments the pump photon fluxes (f_p) were 1.3 × 10¹⁰ and 3.3 × 10¹⁰ photons per cm² per pulse for QD1 and QD2, respectively. The size-dependent absorption cross-sections (σ_a) of CsPbBr₃ QDs were reported in ref. 51. The average number of excitons (N) was estimated as: (N) = σ_a × f_p, which is 0.05 and 0.16 for QD1 and QD2, respectively. However, it is important to note that we used circularly polarized photons to address only one of the two-fold degenerate quasiparticle transitions. Therefore, (N) should be further reduced by half, that is, (N) = 0.025 and 0.08 for QD1 and QD2, respectively.

**Preparation of QD–AQ complexes**

The CsPbBr₃ QD–AQ complexes were prepared by adding anthraquinone-2-carboxylic acid powder into the CsPbBr₃ QDs solution, followed by stirring for 30 min and filtration. On the basis of the reported extinction coefficients of QDs (σ_a) and that measured for AQ (~5,500 M⁻¹ cm⁻¹ at 325 nm), there are (on average) ~280 and 220 AQ molecules for each QD1 and QD2, respectively. The solubility of AQ molecules in hexane is negligible, but in the QD–hexane solution, which contained OA and OAm ligands in excess, AQ becomes slightly soluble. Thus, the molecular numbers above are slightly overestimated. Nevertheless, previous nuclear magnetic resonance measurements for similar CsPbBr₃ QD–molecule systems suggest that the majority of acceptor molecules are indeed bound to QD surfaces.

**Femtosecond transient absorption**

Femtosecond transient absorption measurements were carried out using a Pharos femtosecond laser system (Light Conversion; 1,030 nm, full-width at half-maximum 230 fs, 20 W) and Orpheus-HP optical parameter amplifier (Light Conversion)⁴⁶. The repetition frequency of the Pharos femtosecond laser system is tunable from 1 kHz to 100 kHz and was set at 10 kHz for current experiments. The 1,030 nm output laser was split into two beams with an 80/20 ratio. The 80% part was used to pump the optical parameter amplifier to generate a wavelength-tunable pump beam. The remaining 1,030 nm beam from the optical parameter amplifier was focused into a 2-mm-thick BBO crystal to generate a 515 nm tipping beam. A notch filter with a centre wavelength of 514 ± 2 nm and full-width at half-maximum of 17 nm was used to remove 1,030 nm photons from the tipping pulses. The 20% part was further split into two parts with a 75/25 ratio. The 75% part was attenuated with a neutral-density filter and focused into a BBO crystal to generate a 515 nm beam, which was further focused into a sapphire crystal to generate a white-light continuum used as the probe beam. The probe beam was focused with an Al parabolic reflector onto the sample. The probe beam was then collimated and focused into a fibre-coupled spectrometer with a line scan camera and detected at a frequency of 10 kHz.

The intensity of the pump and tipping pulses used in the experiment was controlled by a variable neutral-density filter wheel. The delay between the pump and probe pulses was controlled by a motorized delay line and the delay between the pump and tipping pulses was controlled by a homemade delay line. The pump or tipping beam was chopped by a synchronized chopper at 5 kHz and the absorbance change was calculated with adjacent probe pulses. The probe, pump and tipping beams were focused and spatially overlapped on the sample with spot sizes of 240 μm, 270 μm and 355 μm, respectively (at 1/e² intensity), with the spot sizes measured using the knife-edge method. The pulse durations were ~540 fs at 1/e² intensity. Circular polarizations of the pump, tipping and probe beams were controlled by quarter waveplates. The magnetic field direction was perpendicular to the laser beams, and provided by an electromagnet (EM3; Beijing Jinzhengmao Technology Co.).

Using the pump beam size, the pump power and photon energy, we calculated that in our experiments the pump photon fluxes (f_p) were 1.3 × 10¹⁰ and 3.3 × 10¹⁰ photons per cm² per pulse for QD1 and QD2, respectively. The size-dependent absorption cross-sections (σ_a) of CsPbBr₃ QDs were reported in ref. 51. The average number of excitons (N) was estimated as: (N) = σ_a × f_p, which is 0.05 and 0.16 for QD1 and QD2, respectively. However, it is important to note that we used circularly polarized photons to address only one of the two-fold degenerate quasiparticle transitions. Therefore, (N) should be further reduced by half, that is, (N) = 0.025 and 0.08 for QD1 and QD2, respectively.

**Data availability**

All data are available in the main text or Supplementary Information and can be obtained upon request from the corresponding author. The data are also available via Figshare at https://figshare.com/articles/figure/Data_for_Room-temperature_coherent_optical_manipulation_of_hole_spins_in_solution-grown_perovskite_quantum_dots_/21378075. Source data are provided with this paper.

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Author contributions
K.W. conceived the idea and designed the project. X.L. and Y.H. synthesized the samples, performed the spectroscopy with the help of J.Z. and analysed the data. K.W. wrote the manuscript with input from all authors. X.L. and Y.H. contributed equally to this work.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Kaifeng Wu.

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