Ultra-narrow optical linewidths in rare-earth molecular crystals

https://doi.org/10.1038/s41586-021-04316-2

Received: 21 May 2021

Accepted: 7 December 2021

Published online: 9 March 2022

Check for updates

Diana Serrano^{1,8}, Senthil Kumar Kuppusamy^{2,3,8}, Benoît Heinrich⁴, Olaf Fuhr^{3,5}, David Hunger^{2,6}, Mario Ruben^{2,3,7} Philippe Goldner^{1 \cong}

Rare-earth ions (REIs) are promising solid-state systems for building light-matter interfaces at the quantum level^{1,2}. This relies on their potential to show narrow optical and spin homogeneous linewidths, or, equivalently, long-lived quantum states. This enables the use of REIs for photonic quantum technologies such as memories for light, optical-microwave transduction and computing³⁻⁵. However, so far, few crystalline materials have shown an environment quiet enough to fully exploit REI properties. This hinders further progress, in particular towards REI-containing integrated nanophotonics devices^{6,7}. Molecular systems can provide such capability but generally lack spin states. If, however, molecular systems do have spin states, they show broad optical lines that severely limit optical-to-spin coherent interfacing⁸⁻¹⁰. Here we report on europium molecular crystals that exhibit linewidths in the tens of kilohertz range, orders of magnitude narrower than those of other molecular systems. We harness this property to demonstrate efficient optical spin initialization, coherent storage of light using an atomic frequency comb, and optical control of ion-ion interactions towards implementation of quantum gates. These results illustrate the utility of rare-earth molecular crystals as a new platform for photonic quantum technologies that combines highly coherent emitters with the unmatched versatility in composition, structure and integration capability of molecular materials.

REI-doped materials are promising systems for optical quantum technologies. At cryogenic temperatures, REIs doped into high-quality bulk single crystals, such as Y₂SiO₅, show exceptionally narrow optical homogeneous linewidths, equivalent to long quantum coherence lifetimes (T_2) , suitable for building quantum light-matter interfaces². Moreover, REIs can present optically addressable electron and/or nuclear spin degrees of freedom that can be leveraged to efficiently store and process quantum information^{1,11}. These unique properties in the solid state have been used to demonstrate quantum memories for light¹², light-matter teleportation³, and frequency- and time-multiplexed storage¹³. REI-doped crystals are also being actively investigated for optical to microwave conversion⁴ and guantum processing⁵. Besides experiments on high-quality bulk single crystals, strong efforts have recently been launched towards combining REIs with nanophotonic structures¹⁴. This has enabled single-REI detection and control^{6,7}, fast spontaneous-emission modulation¹⁵, lifetime-limited single-photon emission¹⁶ and on-chip optical storage¹⁷. Further developments of these exciting topics are, however, impeded by the difficulty to nanofabricate crystalline host materials that preserve REIs' quantum properties for integration into high-quality nanophotonic devices. This difficulty is faced by many solid-state systems, although promising results have recently been reported (for example, with colour

centres in diamond)^{1,18}. Molecular chemistry is very attractive in this respect because it offers unmatched flexibility in terms of material composition, fine structural tuning and integration into photonic structures, as demonstrated by numerous results obtained with single organic molecules embedded in crystalline host lattices¹⁰. However, most organic molecules studied to date lack a spin degree of freedom. Recently, optically addressable molecular spins were demonstrated^{8,9}. although with limited optical coherence, hindering their use as coherent spin-photon interfaces. Narrow homogeneous linewidths are in effect key to high-fidelity optical spin control in quantum processors⁵ and high-efficiency light-to-spin transfer in long-storage-time quantum memories². Here we introduce REI molecular crystals containing trivalent europium that exhibit optical homogeneous linewidths between 5 and 30 kHz, 3 to 4 orders of magnitude narrower than those of any molecular system^{9,10,19}. This allows us to efficiently exploit the nuclear spin degree of freedom by demonstrating >95% spin initialization into a single level, and coherent optical storage using atomic frequency combs (AFCs). We also harness the narrow optical linewidth of Eu³⁺to demonstrate ion-ion interactions, which are the basis for high-bandwidth two-qubit quantum gates5.

The molecular crystal is composed of a mononuclear Eu^{3+} complex $[Eu(BA)_4(pip)],$ in which BA and pip stand for benzoylacetonate

¹Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, Paris, France. ²Institute for Quantum Materials and Technologies (IQMT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. ³Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. ⁴Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS-Université de Strasbourg, Strasbourg, France. ⁵Karlsruhe Nano Micro Facility (KIMF), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. ⁶Physikalisches Institut, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. ⁷Centre Européen de Sciences Quantiques (CESQ), Institut de Science et d'Ingénierie Supramoléculaire (ISIS), Université de Strasbourg, Strasbourg, France. ⁸These authors contributed equally: Diana Serrano, Senthil Kumar Kuppusamy. ⁵⁶e-mail: diana.serrano@chimieparistech.psl.eu; senthil.kuppusamy2@kit.edu; mario.ruben@kit.edu; philippe.goldner@chimieparistech.psl.eu



Fig. 1|**Material and low-temperature optical spectroscopy. a**, X-ray crystal structure of the Eu³⁺ complex. The counter cation, omitted for clarity, is shown in Extended Data Fig. 1. Grey, carbon; white, hydrogen; pink, europium; red, oxygen. **b**, Eu³⁺ PL spectrum showing characteristic ${}^{5}D_{0} \rightarrow {}^{7}F_{J}(J = 0 - 4)$ transitions (see inset). All of the following results were obtained on the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$

transition (in red). **c**, ${}^7F_0 \rightarrow {}^5D_0$ absorption line recorded on a 500-µm-thick powder sample. Centre wavelength: 580.3778 nm (vacuum). FWHM, full-width at half-maximum. **d**, ${}^5D_0 \rightarrow {}^7F_J$ (J = 1-4) fluorescence decay. Red line: single exponential fit to data giving a 5D_0 population lifetime of $T_{1.opt} = 540$ µs.

and piperidin-1-ium, respectively²⁰ (Fig. 1a and Extended Data Fig. 1). For clarity, it is referred to as the Eu³⁺ complex hereafter. The complex crystallized in the $P2_1/n$ space group, belonging to the monoclinic crystal system, with a crystal lattice composed of anionic $[Eu(BA)_4]^-$ and cationic piperidin-1-ium units (Extended Data Fig. 1, see Supplementary Section 1 for more details). The all-oxygen coordination environment around the Eu³⁺ centre is best described as a biaugmented trigonal prism with the help of a continuous shape measure calculation²¹. The point group symmetry around the Eu³⁺ centre is assigned to $C_{2\mu}$ as inferred from the continuous shape measure calculation and luminescence spectrum depicted in Fig. 1b (see Supplementary Section 2). All experiments discussed in the following were performed on microcrystalline powders with grain sizes of at least 50 nm (see Supplementary Section 1). The Eu³⁺ complex showed high physical and chemical stability over time. Repeated cooling cycles had no noticeable effects on optical properties, and no photodegradation was observed at low temperature or under high laser intensity (Extended Data Fig. 2).

Figure 1b shows the emission spectrum of the Eu³⁺ complex in which the characteristic lines of trivalent europium are observed²¹. We focused on the ⁷F₀ \rightarrow ⁵D₀ transition at 580.3778 nm (vacuum) as this transition is associated with narrow linewidths in crystals such as Y₂SiO₅ (ref. ²²). Moreover, it enables optical control of ground-state nuclear spins, an important feature for applications in quantum technologies. Transmission experiments revealed a ⁷F₀ \rightarrow ⁵D₀ inhomogeneous linewidth (Γ_{inh}) of 6.6 GHz, corresponding to 0.007 nm (Fig. 1c). This low value, together with a Lorentzian absorption profile, is typical of high-crystalline-quality samples with low disorder²³ (Supplementary Table 12). Strong absorption was observed in a 500-µm-thick powder as a result of the stoichiometric composition of the molecular crystal

and light scattering inside the powder. The ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ oscillator strength is estimated to be 6.7×10^{-9} (see Supplementary Section 4.2). Fluorescence decay experiments led to a lifetime value $T_{1,opt}$ of 540 µs for the ${}^{5}D_{0}$ level (Fig. 1d). This sets a limit of only $1/2\pi T_{1,opt} = 295$ Hz on the optical homogeneous linewidth (Γ_{h}).

The photon echo (PE) technique, similar to Hahn's spin echo experiment, enables accurate assessment of narrow homogeneous linewidths^{2,24}. Owing to its high sensitivity, it can be applied to powders²⁵, allowing us to measure the optical coherence lifetime, or quantum-state lifetime T_2 , of the ${}^5D_0 \leftrightarrow {}^7F_0$ transition in the Eu ${}^{3+}$ complex (Fig. 2a). $\Gamma_{\rm h} = 1/\pi T_2$ was found to be equal to 30.2 ± 0.6 kHz, markedly lower than values in the tens of megahertz range reported for transition metal ions²⁶, a previously reported Eu³⁺ complex⁹ and single molecules¹⁰, although in the last case, lifetime-limited linewidths have been observed. The Eu³⁺ linewidth in the complex is indeed comparable to those measured in 0.3% Eu³⁺:Y₂O₃ nanoparticles¹⁴ and even in some bulk stoichiometric crystals such as EuP₅O₁₄ (ref. ²⁷), although still broader than the narrowest reported linewidths²³. Supplementary Table 12 gathers data for a range of materials for a more comprehensive comparison. Line broadening was further explored using stimulated PEs, showing a increase in $\Gamma_{\rm h}$ of \approx 105 kHz for 1 ms delay (Fig. 2b and Supplementary Section 4.2).

Insights into dephasing mechanisms occurring in the complex were also obtained from the evolution of Γ_h with temperature T, measured by two-pulse PE and spectral hole burning (SHB; Fig. 2c). Two regimes were identified: for temperatures below 3.5 K, dephasing is dominated by coupling to two-level systems (TLSs) and Γ_h increases linearly with T(Fig. 2c, inset)²⁸; above 3.5 K, the exponential increase of Γ_h is attributed to quasi-localized low-frequency modes (LFMs)²⁹. Data were modelled



Fig. 2 | **Ultra-narrow optical homogeneous linewidths. a**, Two-pulse PE decay for the ⁷F₀ \rightarrow ⁵D₀ transition (pulse sequence shown in inset). Red line: exponential fit to data giving $T_2 = 10.5 \pm 0.2 \,\mu$ s or $\Gamma_h = 1/\pi T_2 = 30.2 \pm 0.6 \,\text{kHz}$. **b**, Γ_h as a function of waiting time (τ_w) measured by three-pulse PE. Red line: fit using a spectral diffusion model yielding a flip rate $R = 2.9 \pm 0.8 \,\text{kHz}$ and a width $\Gamma_{\text{sD}} = 154 \pm 16 \,\text{kHz}$ (see Supplementary Section 4.3 for more details). **c**, Temperature dependence of Γ_h measured by two-pulse PE (blue dots) and SHB (black dots). Red line: fit to a model including contributions from TLSs and

using the expression $\Gamma_{\rm h}(T) = \Gamma_0 + \Gamma_{\rm TLS} + \Gamma_{\rm LFM}$, in which $\Gamma_{\rm TLS} = \alpha_{\rm TLS}T$ and $\Gamma_{\rm LFM} \approx \alpha_{\rm LFM} \exp(-\Delta E_{\rm LFM}/k_{\rm B}T)$, with $k_{\rm B}$ being the Boltzmann constant. The best fit gave a TLS rate $\alpha_{TLS} = 15 \pm 5$ kHz K⁻¹, as observed in some REI-doped crystals²⁸, and an LFM transition energy $\Delta E_{\text{LFM}} = 580 \text{ GHz}$ (19 cm⁻¹), in the range reported for single molecules²⁹. The homogeneous linewidth extrapolated to 0 K (Γ_0) is estimated at 8 ± 4 kHz. This remaining dephasing could be due to $Eu^{3+}-Eu^{3+}$ interactions²², as the crystal has a high Eu³⁺ concentration, $C_{\text{Eu}} = 9.6 \times 10^{20}$ ions per cm³. To investigate this effect, an optically inactive REI, Y³⁺, was introduced into the crystal to reduce C_{Fu} . Figure 2d shows two-pulse PE decays in a series of diluted crystals. The non-exponential decays may indicate distinct environments for the Eu³⁺ ions in these complexes. Increasing coherence lifetimes with decreasing C_{Eu} are observed, especially for the long decay components (Fig. 2d, inset), confirming a contribution of Eu³⁺-Eu³⁺ interactions to dephasing. At the highest dilution investigated here (95%; that is, 5% Eu³⁺ content), we found a 1/e decay time $T_2 = 25 \,\mu\text{s}$ (that is, $\Gamma_h = 12.7 \,\text{kHz}$). Remarkably, in this sample, PEs could be detected even after evolution times of 300 µs, corresponding to a long decay component of $T_2 = 68 \pm 4 \,\mu s \,(\Gamma_h = 4.6 \pm 0.2 \,\text{kHz})$ (inset of Fig. 2d and Extended Data Fig. 3).

Narrow optical linewidths are key to efficiently address REI spins, which enabled detailed investigations of Eu^{3+} nuclear spin states in the complex. First, the nuclear spin structure was determined for the ${}^{5}D_{0}$ excited state and ${}^{7}F_{0}$ ground state by SHB in the stoichiometric



quasi-localized LFMs (see text and Supplementary Section 4.3). Inset: zoom on lower temperature range. **d**, PE decays from Y^{3*} -diluted complexes showing T_2 increase with decreasing Eu^{3*} concentration. Red line: single (non-diluted crystals) and double (diluted crystals) exponential decay fits to data. Inset: 1/e echo amplitude decay time T_2 (black dots) and long T_2 component from double exponential fits (blue dots) as a function of Eu^{3*} concentration. Error bars in **b**, **c** and the inset of **d** represent one standard deviation of uncertainty.

complex, which is isotopically enriched in ¹⁵¹Eu³⁺. At zero magnetic field, it consists of three doubly degenerate levels split by quadrupolar interaction²², giving rise to a complex SHB spectrum after optical pumping. Thanks to the narrow optical linewidth, well-resolved spectral features could be recorded and analysed (Fig. 3a). This allowed us to assign ground- and excited-state splitting energies (Fig. 3b, left), and transition branching ratios between nuclear spin levels (Supplementary Fig. 12). The same study was performed on a sample with natural abundance, from which splitting energies and transition branching ratios were determined for the ¹⁵³Eu³⁺ isotope (Supplementary Fig. 13). Notably, the obtained branching ratios show the existence of efficient three-level lambda systems for both isotopes in the Eu³⁺ complex, an important requirement for all-optical spin control³⁰.

We then probed the dynamics of ground-state spin populations by monitoring the spectral hole depth as a function of the time delay between the burn and readout pulses (Fig. 3c). Two distinct decay components can be observed with relaxation times estimated to be 430 ± 100 ms and 5.0 ± 0.5 min. Although Eu³⁺ spins often have much longer relaxation times (see Supplementary Table 12), the nuclear spin levels in the complex can be used as shelving states for at least hundreds of milliseconds. Such long times enable efficient optical manipulation of the spin population. As an example, we initialized ions into one nuclear spin level using two-colour laser pulses at frequencies v_1 and v_2 . This simultaneously depletes the $|\pm 5/2_{\sigma}\rangle$ and $|\pm 3/2_{\sigma}\rangle$ ground-state



Fig. 3 | **Optically addressable nuclear spins. a**, SHB experimental spectrum of the ¹⁵¹Eu³⁺ stoichiometric complex (blue) compared to simulation (red). **b**, Left: ¹⁵¹Eu³⁺ ground- and excited-state nuclear spin splittings. Right: scheme of spin initialization by two-colour optical pumping. **c**, Hole decay as a function of delay between the burn and readout pulses (see Methods). Red line: double exponential fit yielding spin relaxation times $T_{1,spin}$ of 430 ± 100 ms and

spin levels and transfers population into $|\pm 1/2_g\rangle$ (right panel of Fig. 3b and Supplementary Fig. 14). As displayed in Fig. 3d, nearly full transparency could be induced at v_1 and v_2 , which translates to initialization of 95% of the spin population into a single level. This also proves that efficient spectral tailoring is possible in the Eu³⁺ complex, an essential feature for many quantum memory and processing protocols based on REIs^{5,12}.

We next used the narrow optical linewidths of Eu³⁺ molecular crystals to demonstrate coherent optical storage and controlled ion-ion interactions. In the first case, we used the AFC protocol¹² to store a light pulse in the molecular crystal. This protocol enables quantum memories based on an ensemble of ions with very low output noise and multiplexed storage, important assets for long-distance quantum communications. We first made use of the efficient optical pumping achieved in the Eu³⁺ complex to create an AFC spanning a 6 MHz range, with three 0.9-MHz-wide teeth separated by 1.75 MHz (Fig. 4a). A storage experiment was then performed with a 0.15-µs-long input pulse overlapping the AFC structure. As shown in Fig. 4b, the output pulse is observed at a delay $t_s = 0.57 \,\mu s$ after the partially transmitted input pulse, in perfect agreement with the tooth spacing as $1/t_s = 1.75$ MHz (ref. ¹²). By varying the tooth spacing and adapting the input pulse length to keep an identical spectral overlap with the comb, output pulses were observed up to about 1 µs storage time, clearly confirming the AFC process (Fig. 4b, inset). Storage efficiency, defined as the ratio between input and output pulse intensities, was 0.86% for a storage time $t_s = 0.57 \,\mu s$, in agreement with theory (see Supplementary Section



5.0 ± 0.5 min. Error bars represent one standard deviation of uncertainty. **d**, Initialization to a single spin level by two-colour optical pumping over a bandwidth of 3 MHz. Applying the pumping scheme shown in **b** (right), population is transferred from $|\pm 3/2_g\rangle$ and $|\pm 5/2_g\rangle$ levels (deep holes at v_1 and v_2), to $|\pm 1/2_g\rangle$ (increased absorption, or anti-hole, at v_3). T = 1.45 K.

6.1). This efficiency could be boosted up to 100% in an optical cavity³¹. This could be achieved by crystallizing the Eu^{3+} complex directly on a cavity mirror. Storage times up to several tens of microseconds could also be obtained by creating narrower teeth¹² with a suitable laser, given the narrow homogeneous linewidths and limited spectral diffusion in the Eu^{3+} complex.

We finally investigated controlled interactions between Eu^{3+} ions. The scheme we used is based on the difference in permanent electric dipole moments between Eu^{3+} ground ($^{7}F_{0}$) and excited ($^{5}D_{0}$) states 32 . This difference occurs when Eu^{3+} ions sit in a low-symmetry site, which is the case in our molecular crystal (C_{2v} site symmetry). When a control ion is excited, the electric field it produces changes, causing a shift in transition frequency for a nearby target ion through the linear Stark effect. This mechanism is the basis for two-qubit gates and qubit readout in some REI-based quantum computing proposals⁵. However, to be useful, ion–ion interactions must be significantly larger than the optical homogeneous linewidth, a condition well matched by our highly concentrated Eu^{3+} complex with 30 kHz linewidth.

Target and control ions were chosen at different frequencies within the absorption line (Fig. 1c) to allow for independent excitation and monitoring. As a result of the distribution of distances and orientations and therefore interaction strengths between Eu³⁺ ions, the excitation of control ions results in an additional line broadening Γ_c for target ions, as detailed in Supplementary Section 6.2 (ref. ³³). Γ_c can be conveniently measured by monitoring the amplitude of a PE produced by target ions while an extra pulse excites the control ions (Supplementary Fig. 15b).



Fig. 4 | **Coherent light storage and optically controlled ion-ion interactions. a**, AFC created by optical pumping within the inhomogeneously broadened ⁷F₀ \rightarrow ⁵D₀ line. The 0.9-MHz-wide teeth are separated by 1.75 MHz and span 6 MHz. Blue line: input pulse spectrum. Centre wavelength 580.3730 nm. **b**, Coherent storage of a 0.15-µs-long input pulse (blue line) using the AFC structure in **a**. The output pulse appears at 0.57 µs (solid red line, intensity ×3) with a storage efficiency of 0.86% (see text). Part of the input pulse is directly transmitted and not stored (dashed line at 0 µs). Inset: variable storage times *t*_s obtained by changing AFC tooth frequency separation *Δ*. Input pulse lengths were adapted to keep identical spectral overlap with AFCs. **c**, PE

We first investigated the effect of changing the evolution time (t_{evol}) between the control pulse and the echo, as shown in Fig. 4c. In this case, the echo amplitude varies as $\exp(-\pi\Gamma_c t_{evol})$ (ref. ³³). A fit to the experimental data yields $\Gamma_c = 14.5 \pm 1 \text{ kHz}$, in gualitative agreement with expected Eu³⁺-Eu³⁺ electric dipole interactions (see Supplementary Section 6.2) and previous experiments in non-molecular REI-doped crystals³³. It also provides an upper bound to the ion-ion interaction contribution in the measurements of $\Gamma_{\rm h}$ by two-pulse PEs (see Supplementary Section 4.3). We further confirmed this analysis by varying the control pulse intensity I_c . In the weak excitation regime, $\Gamma_{\rm c}$ is proportional to the fraction of excited control ions (p), with $p \propto I_{\rm c}$. We indeed observed the predicted exponential decay of the echo amplitude with increasing p, as displayed in Fig. 4d. Finally, the control pulse frequency was varied over several tens of megahertz with fixed t_{evol} and p. No significant change in echo amplitude was observed, ruling out a direct light-induced frequency shift of target ions, the so-called a.c. Stark shift¹⁷ (Fig. 4e). We therefore conclude that qubit gate and readout schemes based on electric dipole-dipole interactions could be implemented in the molecular crystal. As a result of the high Eu³⁺ concentration and narrow linewidth, we estimate that one ion could control thousands of target ions, while the large inhomogeneous to homogeneous linewidth ratio (2.2 × 105) enables individual addressing of a large number of single ions (see Supplementary Section 6.2). These are useful properties for scaling up REI-based quantum processors5.



amplitude of target ions (at frequency v_a) as a function of evolution time t_{evol} after excitation of control ions (at $v_b = v_a - 20$ MHz and p = 0.16; see below). Red line: exponential fit to data giving a broadening of the target ions' linewidth by the control ions of $\Gamma_c = 14.5 \pm 1$ kHz (see text). **d**, PE amplitude of target ions as a function of control ions' excitation probability p, normalized to the maximum value reached experimentally ($t_{evol} = 3.5 \,\mu$ s). Red line: exponential fit. **e**, PE amplitude of target ions as a function of control pulse detuning (p = 0.16, $t_{evol} = 17 \,\mu$ s). All experiments were performed at 1.45 K in the stoichiometric ¹⁵¹Eu³⁺-enriched complex. Error bars represent one standard deviation of uncertainty.

The Eu³⁺ complex investigated in this study is a very promising platform for optical quantum technologies as a robust system with narrow linewidth and long-lived optically addressable spins. Furthermore, a significant decrease in optical homogeneous linewidth could be obtained by lowering the temperature, tuning the REI concentration and optimizing synthesis to decrease residual defects or impurities. In such compounds, interactions with host nuclear spins such as ¹H or ¹³C could become the dominant dephasing mechanisms, which can be reduced using specific isotopes with lower or zero magnetic moments³⁴. This could also be useful to obtain spin states with long coherence lifetimes, a property that remains to be measured in our samples. The huge possibility in molecular design also opens the way to accurate engineering of the ligand field acting on europium and more generally other REIs of interest for quantum technologies, such as Er³⁺or Yb³⁺. This would allow optimization of transition strengths and frequencies for optimal coupling to light, tuning of electronic and spin level structures, and coupling to molecular vibrations for long coherence lifetimes. Complexes containing several REIs at close distance can also be synthesized, which would enable high-density optically addressable qubit architectures, as shown with REI magnetic molecules in the microwave range³⁵. Developments towards applications in quantum technologies could greatly benefit from integration of molecular crystals into nanophotonic structures. For example, high-quality and small-mode-volume optical cavities can dramatically enhance coupling of REIs with light, enabling efficient emission from nominally weak transitions^{6,7,15}. This would be

facilitated by the broad range of synthesis, functionalization and deposition methods that are available for molecular complexes^{10,34}, as well as the scalable production of large amounts of identical molecules. REI molecular crystals could therefore emerge as a versatile platform for highly coherent light–matter–spin quantum interfaces for developing applications in quantum communications and processing and fundamental studies in quantum optics.

Online content

Any methods, additional references, Nature Research 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/s41586-021-04316-2.

- Awschalom, D. D., Hanson, R., Wrachtrup, J. & Zhou, B. B. Quantum technologies with optically interfaced solid-state spins. *Nat. Photon.* 12, 516–527 (2018).
- Goldner, P., Ferrier, A. & Guillot-Noël, O. in Handbook on the Physics and Chemistry of Rare Earths Vol. 46 (eds Bünzli, J.-C. G. & Pecharsky, V. K.) 1–78 (Elsevier, 2015).
- Bussières, F. et al. Quantum teleportation from a telecom-wavelength photon to a solid-state quantum memory. Nat. Photon. 8, 775–778 (2014).
- Bartholomew, J. G. et al. On-chip coherent microwave-to-optical transduction mediated by ytterbium in YVO₄. Nat. Commun. 11, 3266 (2020).
- Kinos, A. et al. Roadmap for rare-earth quantum computing. Preprint at https://arxiv.org/ abs/2103.15743 (2021).
- Kindem, J. M. et al. Control and single-shot readout of an ion embedded in a nanophotonic cavity. *Nature* 580, 201–204 (2020).
- Chen, S., Raha, M., Phenicie, C. M., Ourari, S. & Thompson, J. D. Parallel single-shot measurement and coherent control of solid-state spins below the diffraction limit. *Science* 370, 592–595 (2020).
- Bayliss, S. L. et al. Optically addressable molecular spins for quantum information processing. Science 370, 1309–1312 (2020).
- Kumar, K. S. et al. Optical spin-state polarization in a binuclear europium complex towards molecule-based coherent light-spin interfaces. *Nat. Commun.* 12, 2152 (2021).
- Toninelli, C. et al. Single organic molecules for photonic quantum technologies. Nat. Mater. 20, 1615–1628 (2021).
- Zhong, M. et al. Optically addressable nuclear spins in a solid with a six-hour coherence time. Nature 517, 177–180 (2015).
- de Riedmatten, H., Afzelius, M., Staudt, M. U., Simon, C. & Gisin, N. A solid-state lightmatter interface at the single-photon level. *Nature* 456, 773–777 (2008).
- Seri, A. et al. Quantum storage of frequency-multiplexed heralded single photons. Phys. Rev. Lett. 123, 080502 (2019).

- 14. Zhong, T. & Goldner, P. Emerging rare-earth doped material platforms for quantum nanophotonics. *Nanophotonics* **8**, 2003–2015 (2019).
- Casabone, B. et al. Dynamic control of Purcell enhanced emission of erbium ions in nanoparticles. Nat. Commun. 12, 3570 (2021).
- Zhong, T. et al. Optically addressing single rare-earth ions in a nanophotonic cavity. Phys. Rev. Lett. 121, 183603 (2018).
- Zhong, T. et al. Nanophotonic rare-earth quantum memory with optically controlled retrieval. Science 357, 1392–1395 (2017).
- Bhaskar, M. K. et al. Experimental demonstration of memory-enhanced quantum communication. *Nature* 580, 60–64 (2020).
- Zirkelbach, J. et al. Partial cloaking of a gold particle by a single molecule. Phys. Rev. Lett. 125, 103603 (2020).
- Melby, L. R., Rose, N. J., Abramson, E. & Caris, J. C. Synthesis and fluorescence of some trivalent lanthanide complexes. J. Am. Chem. Soc. 86, 5117–5125 (1964).
- Binnemans, K. Interpretation of europium (III) spectra. Coord. Chem. Rev. 295, 1–45 (2015).
- Könz, F. et al. Temperature and concentration dependence of optical dephasing, spectral-hole lifetime, and anisotropic absorption in Eu³⁺:Y₂SiO₅. *Phys. Rev. B* 68, 085109 (2003).
- Thiel, C. W., Böttger, T. & Cone, R. L. Rare-earth-doped materials for applications in quantum information storage and signal processing. J. Lumin. 131, 353–361 (2011).
- Abella, I. D., Kurnit, N. A. & Hartmann, S. R. Photon echoes. *Phys. Rev.* 141, 391 (1966).
 Perrot. A. et al. Narrow optical homogeneous linewidths in rare earth doped nanocrystr
- Perrot, A. et al. Narrow optical homogeneous linewidths in rare earth doped nanocrystals. *Phys. Rev. Lett.* 111, 203601 (2013).
 Piscan H. Hole huming appendic score of scored instance compounds. *Coard. Cham. Pay.*
- Riesen, H. Hole-burning spectroscopy of coordination compounds. Coord. Chem. Rev. 250, 1737–1754 (2006).
- Shelby, R. & Macfarlane, R. M. Frequency-dependent optical dephasing in the stoichiometric material EuP₅O₁₄. Phys. Rev. Lett. 45, 1098–1101 (1980).
- Flinn, G. P. et al. Sample-dependent optical dephasing in bulk crystalline samples of Y₂O₃:Eu³⁺. *Phys. Rev. B* **49**, 5821 (1994).
- Kozankiewicz, B. & Orrit, M. Single-molecule photophysics, from cryogenic to ambient conditions. Chem. Soc. Rev. 43, 1029–1043 (2014).
- 30. Serrano, D., Karlsson, J., Fossati, A., Ferrier, A. & Goldner, P. All-optical control of
- long-lived nuclear spins in rare-earth doped nanoparticles. *Nat. Commun.* 9, 2127 (2018).
 Afzelius, M. & Simon, C. Impedance-matched cavity quantum memory. *Phys. Rev. A* 82, 022310 (2010).
- Macfarlane, R. M. Optical Stark spectroscopy of solids. J. Lumin. 125, 156–174 (2007).
- Altner, S. B., Mitsunaga, M., Zumofen, G. & Wild, U. P. Dephasing-rephasing balancing in photon echoes by excitation induced frequency shifts. *Phys. Rev. Lett.* 76, 1747–1750 (1996).
- 34. Wernsdorfer, W. & Ruben, M. Synthetic Hilbert space engineering of molecular qudits: isotopologue chemistry. *Adv. Mater.* **31**, 1806687 (2019).
- Godfrin, C. et al. Operating quantum states in single magnetic molecules: implementation of Grover's quantum algorithm. *Phys. Rev. Lett.* **119**, 187702 (2017).

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s), under exclusive licence to Springer Nature Limited 2022

Methods

Preparation of the microcrystalline powder form of the ${\rm Eu}^{\rm 3+}$ complex

The europium complex discussed in this study was prepared in several forms including a stoichiometric natural abundance version, a series of yttrium-diluted versions and an isotopically (151Eu³⁺) enriched version. This was achieved by using a slightly modified procedure to that reported by Melby et al.²⁰. In a typical procedure, 1-phenylbutane-1,3-dione, hereafter referred to as ligand, (1.3 g, 8 mmol) was added to 20 ml of ethanol at 75 °C and dissolved by stirring. To the ligand solution, piperidine (0.8 ml, 8 mmol) was added, and the solution was stirred for 15 min. To the pale-yellow solution of the deprotonated ligand, EuCl₂·6H₂O (732 mg, 2 mmol) dissolved in 10 ml water was added. After the completion of the addition, heating was switched off, and the reaction mixture was stirred at room temperature for 24 h, yielding a half-white crystalline precipitate of the complex. The precipitate was filtered, washed with 50 ml ethanol several times, and dried under reduced pressure overnight. See Supplementary Section 1 for more details, including X-ray analyses and discussions. All optical experiments reported in the main text were performed on either the stoichiometric isotopically enriched complex or the Y³⁺-diluted complexes.

Low-temperature optical spectroscopy setup

Optical absorption, photoluminescence (PL) decays, PE and SHB measurements were performed in a He bath cryostat (Janis SVT-200) under resonant excitation of the ${}^5D_0 \leftrightarrow {}^7F_0$ transition of Eu $^{3+}$. The excitation source was a tunable continuous-wave dye laser (Sirah Matisse DS) with \approx 300 kHz linewidth. Temperature-dependent measurements were performed by tuning the He gas pressure (T < 4 K) and using a built-in resistance as a heater (T > 4 K). The temperature of the sample holder was monitored with a Si diode (Lakeshore DT-670). Pulse sequences were created using an acousto-optic modulator (AA Optoelectronic MT200-B100A0, 5-VIS, 200 MHz central frequency), in the double-pass configuration, driven by an arbitrary waveform generator (Agilent N8242A) with a 625 megasamples per second sampling rate.

The crystalline powders were placed in a home-built sample holder made of brass. This holder is composed of five individual sample containers that have front and rear optical access through glass windows (Supplementary Fig. 8). Each container was filled with \approx 5 mg of powder, forming slabs of about 500 µm in thickness. The excitation beam was focused on the containers' front openings by a 75-mm-focal-length lens placed in front of the cryostat window. The excitation beam and lens were vertically and/or horizontally translated to study one sample after another during measurements. Light scattered by the powders and transmitted through the back openings was collected by a lens sitting outside the cryostat as shown in Supplementary Fig. 9. Signals were detected with avalanche photodiodes (Hammamatsu C5460 with 10 MHz bandwidth for SHB, and Thorlabs 110 A/M with 50 MHz bandwidth for all other measurements).

PL measurements at 15 K were carried out for the isotopically purified ¹⁵¹Eu³⁺ complex using a closed-cycle cold-finger cryostat. The ⁵D₀ level was resonantly excited at 580.4 nm with a tunable optical parametric oscillator pumped by a Nd³⁺ YAG Q-switched laser (Ekspla NT342BSH, 6 ns pulse length and 10 Hz repetition rate). Spectra were recorded using an Acton SP2300 spectrometer equipped with an holographic grating with 1,200 grooves per mm and an ICCD camera (Princeton Instruments). PL decays were recorded at low temperature for the ¹⁵¹Eu³⁺ complex (Fig. 1d) and Y³⁺-diluted complexes after a single pulse (1 ms long), under resonant excitation of the ⁵D₀ level, yielding comparable decay curves and population lifetimes ($T_{Lopt} \approx 540 \ \mu$ s) for all samples.

Optical absorption

Optical depth (αL) as a function of excitation wavelength (Supplementary Fig. 10) was measured in transmission mode for the ¹⁵¹Eu³⁺ complex

at 1.45 K. αL was calculated as $-\ln(I_{\text{online}}/I_{\text{offline}})$, with I_{online} and I_{offline} being the scattered laser intensities transmitted through the crystalline powder at the optical transition wavelength (online) and in a no-absorption region (offline), respectively. The inhomogeneous broadening of the transition (Γ_{inh}) was determined by a Lorentzian fit to the absorption curve as a function of frequency (Fig. 1c).

PE and SHB measurements

Echo amplitudes from two-pulse and three-pulse PE experiments were detected through the fast Fourier transform of the beating between the PE signal and a frequency-detuned laser pulse (heterodyne pulse, with detuning equal to 30 MHz). During measurements, the laser wavelength was scanned over 500 MHz in 1 s to prevent echo signal loss due to SHB. The length and intensity of the $\pi/2$ and π pulses were optimized to obtain maximum PE amplitudes, with typical pulse lengths between 1 and 2 µs, and a laser power before the cryostat of 300 mW. A short-pass filter was set in front of the avalanche photodiode detector to reject the strong PL emission in the Eu³⁺ complexes. The echo amplitude obtained by fast Fourier transformation was averaged over 50 sequences to improve signal-to-noise ratio. For single exponential echo decays, the optical coherence lifetime (T_2) was directly derived as $\exp(-2\tau/T_2)$. Diluted complexes presented non-exponential decays that were described by double exponential decay curves from which we derived short and long T_2 components.

SHB spectra from isotopically (151Eu3+) enriched and natural abundance complexes, both stoichiometric, were obtained by applying a single pulse, referred to as the burn pulse, of 1 ms length and excitation power of 15 mW. After a waiting time of 10 ms, the spectrum was read out with a 2-ms-long scanning pulse with 5 mW power and 200 MHz scanning range around the burning frequency (Supplementary Fig. 11c). The time before readout was set to 10 ms (that is, $T_{1,opt}$) to enable spontaneous relaxation from the optical excited state, followed by progressive trapping into non-pumped nuclear spin levels. The SHB spectra were corrected for the frequency-dependent response of the acousto-optic modulator by dividing by a readout trace obtained with the burn pulse turned off. A series of high-power pulses scanning over 200 MHz was applied at the end of the sequence to reset the ground-state population back to equilibrium. The population lifetime of the ground-state spin levels $(T_{1,spin})$ was determined by monitoring the hole depth as a function of waiting time between the burn and readout pulses. The hole decay curve presents two distinct decay rates, estimated by fitting a double exponential decay to the experimental data (Fig. 3c).

AFC storage

The AFC preparation in the ¹⁵¹Eu³⁺ complex was carried out as follows: absorption was increased in a spectral region of about 9 MHz by burning a corresponding broad hole (spectral pit) about 30 MHz away (Extended Data Fig. 4a) as determined by the nuclear spin splittings. In a second step, population was burned away at regularly spaced frequencies in the high-absorption region yielding an AFC spanning a 6 MHz range with teeth widths of 0.9 MHz and 1.75 MHz separation (Extended Data Fig. 4b). The experiment was performed 4.3 GHz away from the transition peak at 580.370 nm (Supplementary Fig. 10) to reduce absorption and facilitate optical pumping. The input pulse intensity for the AFC efficiency estimation was measured through the spectral pit and corrected for remaining residual absorption (Extended Data Fig. 4a). The full AFC preparation and storage sequence is displayed in Supplementary Fig. 15a.

Data availability

Datasets generated and/or analysed during the current study are available in the Zenodo repository (https://doi.org/10.5281/ zenodo.5652030). Source data are provided with this paper.

Acknowledgements We thank M. Afzelius for useful discussions, and N. Harada and P. Vermaut for assistance during scanning electron microscopy measurements. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement number 820391 (SQUARE) and EUCOR Marie Skłodowska-Curie COFUND project number 847471 (QUSTEC), the French Agence Nationale de la Recherche under grant ANR-20-CEO9-0022 (UltraNanOSpec), the Frontiers Research in Chemistry Foundation CIRFC number 93 "Optically controlled qudits" and KIT Future Fields Project "Optically addressable qubits".

Author contributions P.G., M.R. and D.H. conceived and supervised the project. D.S. and S.K.K. were involved in the conceptual development of the project. S.K.K. and M.R. were responsible for the synthesis and characterization of the isotopologue complexes. B.H. performed powder X-ray diffraction studies and indexed the patterns. O.F. solved the X-ray structure of the

complex. D.S. and P.G. performed the optical experiments and analysed the results. D.S. and P.G. wrote the manuscript with input from all authors.

Competing interests The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41586-021-04316-2.

Correspondence and requests for materials should be addressed to Diana Serrano, Senthil Kumar Kuppusamy, Philippe Goldner and Mario Ruben.

Peer review information Nature thanks David Mills and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available. Reprints and permissions information is available at http://www.nature.com/reprints.



Extended Data Fig. 1 | **Eu**³⁺ **complex preparation and X-ray crystal structure.** Upper: Schematic representation of the preparation of the europium complex discussed in this study. Lower: X-ray crystal structure of the complex. As shown, the piperidin-1-ium cation is involved in hydrogen bonding interactions with two oxygen atoms of benzoylacetonate ligands.



Extended Data Fig. 2 | **Photostability of the Eu³⁺ complex.** ${}^{5}D_{0}$ photoluminescence (PL) intensity under continuous wave excitation measured at 8 K for the ${}^{151}Eu^{3+}$ isotopically enriched complex. The constant PL signal confirms absence of photobleaching. See SI section 3 for more details.



Extended Data Fig. 3 | **2-pulse photon echo decay from the 5% Eu³⁺-95% Y³⁺ diluted complex.** The experimental decay (black circles) was fitted with a double exponential model (red curve) with $T_{2,fax} = 18 \,\mu s$ and $T_{2,slow} = 68 \,\mu s$ decay time constants.



Extended Data Fig. 4 | **Spectral tailoring prior to AFC storage. a**. Spectral pit of 9 MHz dug in the absorption profile at 30 MHz to create a high absorption region at 0 MHz. **b**. Atomic frequency comb (AFC) with teeth of 0.9 MHz separated by 1.75 MHz (finesse *F* = 1.9). The FFT of the storage pulse is

presented over the AFC (blue line) showing good spectral overlap. The input pulse intensity was estimated by sending it through the spectral pit in **a**, taking advantage of the pit's almost full transparency. A correction was made to account for residual absorption.