

Room-Temperature Optically Detected Coherent Control of Molecular Spins

Adrian Mena^{1,2,*}, Sarah K. Mann^{1,*}, Angus Cowley-Semple^{1,*}, Emma Bryan³, Sandrine Heutz³,
Dane R. McCamey², Max Attwood^{3,†} and Sam L. Bayliss^{1,‡}

¹James Watt School of Engineering, *University of Glasgow*, Glasgow, G12 8QQ, United Kingdom

²ARC Centre of Excellence in Exciton Science, School of Physics, *UNSW Sydney*,
Sydney, 2052, New South Wales, Australia

³Department of Materials and London Centre for Nanotechnology, *Imperial College London*,
Prince Consort Road, London, SW7 2AZ, United Kingdom



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Optically interfaced molecular spins are a promising platform for quantum sensing and imaging. Key for such applications is optically detecting coherent spin manipulation at room temperature. Here, using the photoexcited triplet state of organic chromophores (pentacene doped in *p*-terphenyl), we optically detect coherent spin manipulation with photoluminescence contrasts exceeding 15% at room temperature, both in a molecular crystal and thin film. We further demonstrate how multifrequency spin control could enhance such systems. These results open opportunities for room-temperature quantum sensors that capitalize on the versatility of synthetic chemistry.

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Introduction—Electronic spins that can be optically detected and coherently controlled at room temperature have emerged as promising platforms for quantum sensing and imaging. Examples include defects in diamond, such as the nitrogen-vacancy (NV) center [1,2], and defects in silicon carbide [3], and 2D materials [4]. By harnessing the unique properties of quantum mechanics, such systems can extend the capabilities of conventional sensing and imaging. For example, room-temperature optically detected coherent control of electron spins offers advanced detection of quantities ranging from magnetic and electric fields [1,5,6] to temperature [7,8].

Complementary to solid-state defects, electronic spins in molecules are attractive for quantum sensing due to their chemical versatility [9,10]. However, an outstanding challenge for molecular systems is to achieve room-temperature optically detected coherent manipulation—the core functionality underlying systems such as the NV center.

Organic chromophores with photoexcited electronic spins are an attractive system to realize such functionality due to their bright optical transitions, weak spin-orbit

coupling, and mechanisms for spin polarization and readout based on intersystem crossing. Chromophores such as pentacene have enabled remarkable demonstrations, for example, cryogenic single-spin optically detected magnetic resonance [11–13], room-temperature inductively detected coherence [14], high dynamic nuclear polarization [15], and room-temperature masing [16,17]. Recently, continuous-wave optically detected magnetic resonance was reported for pentacene doped in picene at room temperature [18], while the versatility of the acene family (to which pentacene belongs) is highlighted by their ability to be immobilized as monolayers on surfaces [19], or used as dyes for biomedical imaging [20]. More broadly, the rich possibilities optically active molecular spins offer are highlighted by demonstrations spanning structure determination of biomolecules [21–23], electrical spin readout [24], multispin coupling [25], entanglement generation [26,27], and cryogenic defect analogs [28]. However, room-temperature optically detected coherent spin manipulation has remained elusive.

Here, using the photoexcited triplet states of pentacene, doped in a para (*p*)-terphenyl host, we demonstrate room-temperature optically detected coherent spin control. Under ambient conditions, we demonstrate Rabi oscillations with photoluminescence contrasts exceeding 15% in both a molecular crystal and thermally evaporated thin film; optically detected spin coherence on microsecond timescales; as well as multifrequency spin manipulation as a route to enhance photoexcited triplets for quantum sensing. Overall, these results demonstrate the potential for room-temperature quantum sensing and imaging with a molecular platform.

*These authors contributed equally to this work.

†Contact author: m.attwood@imperial.ac.uk

‡Contact author: sam.bayliss@glasgow.ac.uk

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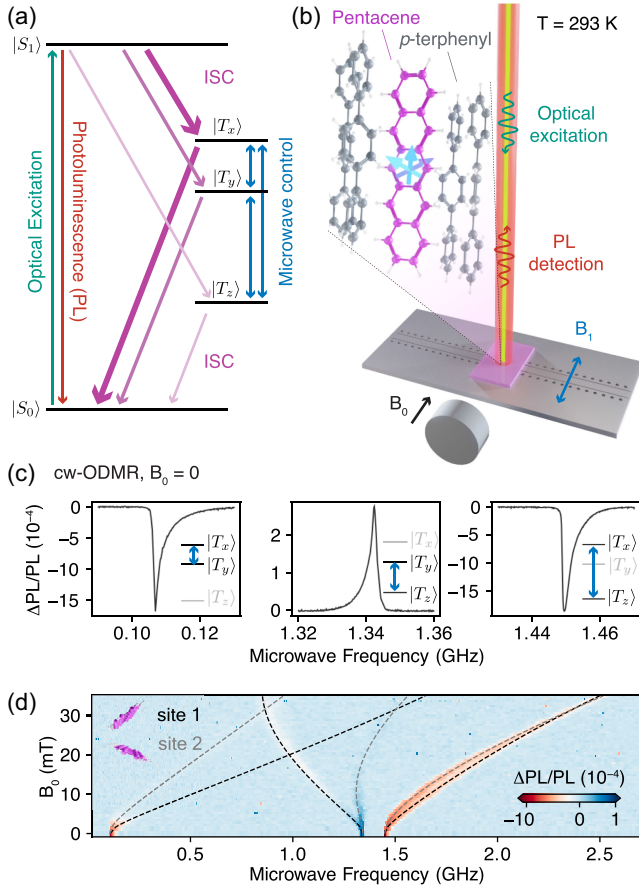


FIG. 1. Room-temperature spin-optical interface in pentacene:*p*-terphenyl. (a) Simplified energy-level diagram for pentacene illustrating the processes involved in spin-polarized triplet formation, microwave spin control, and optical spin detection. (b) Schematic illustration of the experimental setup. (c),(d) Continuous-wave ODMR spectra of a 0.01% doped pentacene:*p*-terphenyl single crystal at (c) zero-field and (d) as a function of magnetic field. Simulations are shown by dashed lines (see Supplemental Material [29] for details).

Room-temperature optical-spin interface—Figure 1(a) summarizes the properties of pentacene that we use for room-temperature pulsed optically detected magnetic resonance (ODMR) (see Supplemental Material [29] for further details). Following optical excitation from the singlet ground state $|S_0\rangle$ to the singlet excited state $|S_1\rangle$, population can either decay back to $|S_0\rangle$, and emit photoluminescence (PL), or undergo intersystem crossing (ISC) to populate the long-lived (depopulation times $\sim 35\text{--}500\ \mu\text{s}$ [30]) spin-1 triplet state with a yield of $\approx 63\%$ [31]. The zero-field splitting removes the degeneracy of the triplet sublevels at zero magnetic field, giving rise to three sublevels, $|T_x\rangle$, $|T_y\rangle$, and $|T_z\rangle$. (The pentacene molecular *X*, *Y*, and *Z* axes are the molecule’s long, short, and out-of-plane axes, respectively.) The zero-field splitting parameters, $D = 1396\ \text{MHz}$ and $E = -53\ \text{MHz}$ [32], give transition frequencies of $107\ \text{MHz}$ ($|T_x\rangle \leftrightarrow |T_y\rangle$),

$1.34\ \text{GHz}$ ($|T_y\rangle \leftrightarrow |T_z\rangle$), and $1.45\ \text{GHz}$ ($|T_x\rangle \leftrightarrow |T_z\rangle$). Anisotropic ISC depopulation rates of the triplet sublevels to $|S_0\rangle$ result in spin-dependent triplet sublevel lifetimes [30]. Irradiation with microwaves resonant with the triplet sublevels’ transition frequencies affects the photoluminescence intensity by transferring populations between longer- and shorter-lived sublevels. This in turn affects the repopulation rate of the $|S_0\rangle$ ground state, and therefore the ability of the molecules to be reexcited and emit PL, thereby enabling optical spin-state detection through ODMR [11,12].

Figure 1(b) shows the key components of our experiment (see Supplemental Material [29] for further details). For spin control, we apply a microwave field (B_1) through a coplanar waveguide. The sample is excited with a laser (520 nm) and we detect the redshifted photoluminescence ($> 600\ \text{nm}$) for spin-dependent readout. Zeeman splitting can be induced with a static magnetic field (B_0 , provided by a permanent magnet).

As a prerequisite for optically detected coherent control, we first measure continuous wave (cw) ODMR of a single crystal of pentacene doped at 0.01% into *p*-terphenyl [Fig. 1(c)]. For the $|T_x\rangle \leftrightarrow |T_y\rangle$ and $|T_x\rangle \leftrightarrow |T_z\rangle$ transitions, we observe an ODMR contrast of approximately -0.2% , while for the $|T_y\rangle \leftrightarrow |T_z\rangle$, we observe a positive contrast, an order of magnitude smaller, of approximately 0.02% (see Supplemental Material [29] for further discussion). The asymmetric ODMR line shapes arise from second-order hyperfine interactions between the triplet spins and the pentacene protons [46]. Figure 1(d) shows the cw-ODMR spectra as a function of an external magnetic field where the transition frequencies shift as a result of Zeeman splitting (the magnetic field was not specifically aligned to the crystal axes). (We note that due to the two inequivalent pentacene lattice sites in *p*-terphenyl, we resolve two sets of resonances for each transition, and the changes in PL contrast with field arise due to the field-induced hybridization between zero-field sublevels.)

Room-temperature optically detected coherent manipulation—We next demonstrate room-temperature optically detected coherent control on the same sample, including Rabi oscillations, Ramsey interferometry, and Hahn echoes. Each of these pulsed experiments follows the same basic sequence. First, we optically initialize (i.e., polarize) the triplet state with a laser pulse, resulting in triplet sublevel populations $P_x:P_y:P_z \approx 0.76:0.16:0.08$ (see Supplemental Material [29] for further discussion) [14]. We then apply a microwave pulse sequence. For spin-dependent optical readout, we incorporate a delay time (tens of microseconds) following microwave manipulation to repopulate the ground state in a spin-dependent fashion due to the different depopulation rates from the triplet sublevels to the ground state $|S_0\rangle$. Photoluminescence collection during a final readout laser pulse probes the singlet ground state, completing the spin readout.

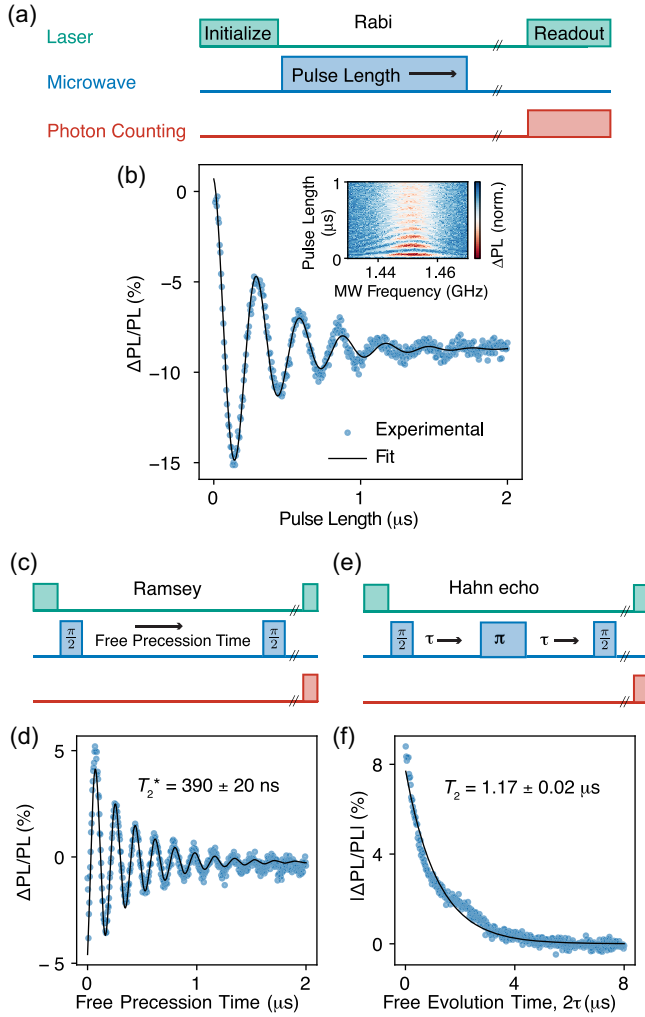


FIG. 2. Optically detected coherent control of molecular spins at room temperature. (All plots are for driving the $|T_x\rangle \leftrightarrow |T_z\rangle$ transition.) (a) Pulse sequence for the Rabi experiment. (b) Rabi oscillations, and Rabi chevron plot showing the PL contrast as a function of microwave frequency and pulse length (inset). (c) Pulse sequence for the Ramsey experiment. (d) Ramsey trace (measured with a 5 MHz detuning) yielding $T_2^* = 390 \pm 20$ ns. (e) Pulse sequence for the Hahn-echo experiment. (f) Hahn-echo measurement yielding $T_2 = 1.17 \pm 0.02$ μ s. Fits for all traces are shown with black lines (see Supplemental Material [29] for details).

All following experiments were performed at zero applied magnetic field.

Focusing on the $|T_x\rangle \leftrightarrow |T_z\rangle$ transition, we drive Rabi oscillations using the pulse sequence in Fig. 2(a), where the microwave pulse length is swept. We observe a PL contrast of approximately 15% [Fig. 2(b)], comparable to that of solid-state defects such as the NV center [2]. We next use a Ramsey sequence [Figs. 2(c) and 2(d), 5 MHz detuning] to optically detect the ensemble dephasing time, $T_2^* = 390 \pm 20$ ns (see Supplemental Material [29] for detuning-dependent Ramsey data), and a Hahn-echo sequence

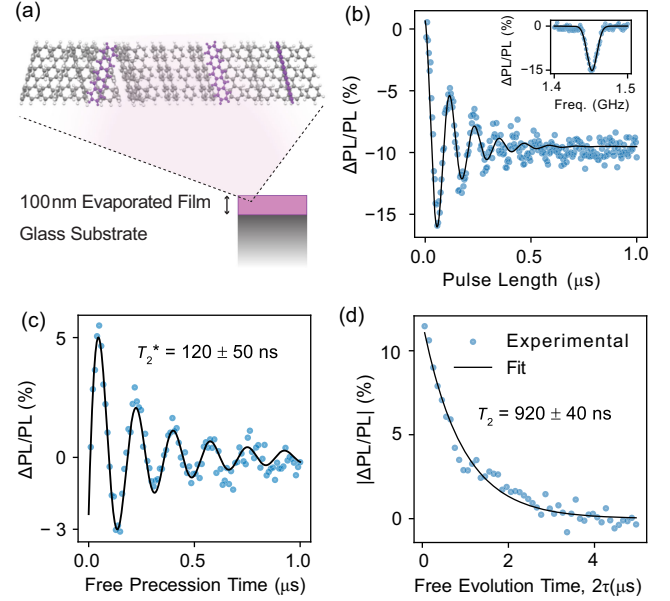


FIG. 3. Optically detected coherent manipulation of a pentacene:*p*-terphenyl thin film under ambient conditions. (a) Schematic of the thin film (0.1% doping concentration) and molecular ordering. (b) Optically detected Rabi oscillations, and pulsed-ODMR spectrum (inset). (c),(d) Ramsey (5 MHz detuning) and Hahn-echo traces. Fits for all traces are shown in black lines.

[Figs. 2(e) and 2(f)] to optically measure the coherence time, $T_2 = 1.17 \pm 0.02$ μ s [Fig. 2(f), exponential fit].

Thin-film measurements—We next demonstrate the opportunities of molecular deposition techniques by extending these results to a thermally evaporated pentacene:*p*-terphenyl thin film. Such films could open up novel opportunities for spin-based quantum sensors due to their ability to be grown with controlled thickness at few-nanometer precision [47], deposited on various surfaces, including flexible substrates [48], and deployed with higher doping concentration ($\sim 1\%$) than crystals [33] while retaining molecular ordering—with pentacene’s long axis preferentially aligning nearly perpendicular to the substrate [49] [Fig. 3(a)]. Here we demonstrate room-temperature optically detected coherent control of a 100 nm film (evaporated onto a glass substrate) with 0.1% pentacene concentration (see Supplemental Material [29] for growth details).

Figure 3(b) shows Rabi oscillations and pulsed ODMR for the $|T_x\rangle \leftrightarrow |T_z\rangle$ transition of the film, demonstrating that this morphology retains high-contrast coherent control, reaching 16%. Figures 3(c) and 3(d) show optically detected Ramsey and Hahn-echo measurements on the same film, yielding $T_2^* = 120 \pm 50$ ns and $T_2 = 920 \pm 40$ ns, comparable to the crystal measurements [Fig. 2(f)], despite the order-of-magnitude higher doping concentration and distinct deposition method.

Multifrequency control—We now outline how multifrequency control could enhance quantum sensing with

photoexcited triplets. In these systems, an attractive scenario would be for two spin sublevels to be highly polarized and long-lived (serving as the sensing qubit), with the third serving as a short-lived readout level, thereby overcoming the trade-off between spin lifetimes and readout efficacy that metastable states present. In planar aromatic hydrocarbons such as pentacene, however, the triplet sublevels which are most rapidly populated through ISC are also typically the ones which are most rapidly depopulated [Fig. 1(a)], and similarly, the sublevel with the slowest depopulation rate also typically has the slowest population rate [50,51]. For example, in pentacene, $|T_x\rangle$ has both the fastest population rate and the fastest depopulation rate, while $|T_z\rangle$ has the slowest population and depopulation rates. This behavior appears to present a trade-off between spin lifetimes and initialization and readout efficiency. However, we can overcome this limitation by coherently controlling multiple spin transitions. Specifically, the more highly populated, but shorter-lived $|T_x\rangle$ population can be transferred through a microwave pulse to the longer-lived levels— $|T_y\rangle$, $|T_z\rangle$ —for control, and then subsequently transferred back to the more rapidly decaying $|T_x\rangle$ sublevel for effective optical readout.

To demonstrate this approach, we use the crystal sample and the pulse sequence shown in Fig. 4(a). A laser pulse is followed by a microwave π pulse on the $|T_x\rangle \leftrightarrow |T_y\rangle$ transition (107 MHz) which transfers the initial (high) $|T_x\rangle$ population to the longer-lived $|T_y\rangle$ state. Following this, a second microwave frequency addresses the $|T_y\rangle \leftrightarrow |T_z\rangle$ transition (1.34 GHz), whose levels have slower depopulation rates than $|T_x\rangle$. A final π pulse on the $|T_x\rangle \leftrightarrow |T_y\rangle$ transition transfers the $|T_y\rangle$ population back onto the more quickly depopulating $|T_x\rangle$ level for more effective optical readout.

Figure 4(b) shows a Rabi oscillation on the $|T_y\rangle \leftrightarrow |T_z\rangle$ transition measured using this multifrequency sequence. For comparison, we also show the signal for single-frequency driving of the $|T_y\rangle \leftrightarrow |T_z\rangle$ transition (i.e., without the $|T_x\rangle \leftrightarrow |T_y\rangle$ π pulses). Multifrequency control gives a PL contrast of 7%, a nearly 20-fold increase over single-frequency driving, which gives a contrast of 0.4% (see Supplemental Material [29]), and allows us to measure a high-contrast Hahn echo on the $|T_y\rangle \leftrightarrow |T_z\rangle$ transition, yielding $T_2 = 1.56 \pm 0.01$ μ s [Fig. 4(c)]. Overall, by separating sensing and readout levels, we anticipate that multifrequency manipulation can be used to overcome the trade-off between efficient optical spin readout and long spin lifetimes that the intrinsic ISC dynamics of organic triplets may appear to present.

Opportunities for quantum sensing—Our results demonstrate key properties required for using molecular spins for room-temperature quantum sensing. For such applications, the key parameters are the combination of (i) proximity to a target, which determines the external field the spins experience, and (ii) their sensitivity to the

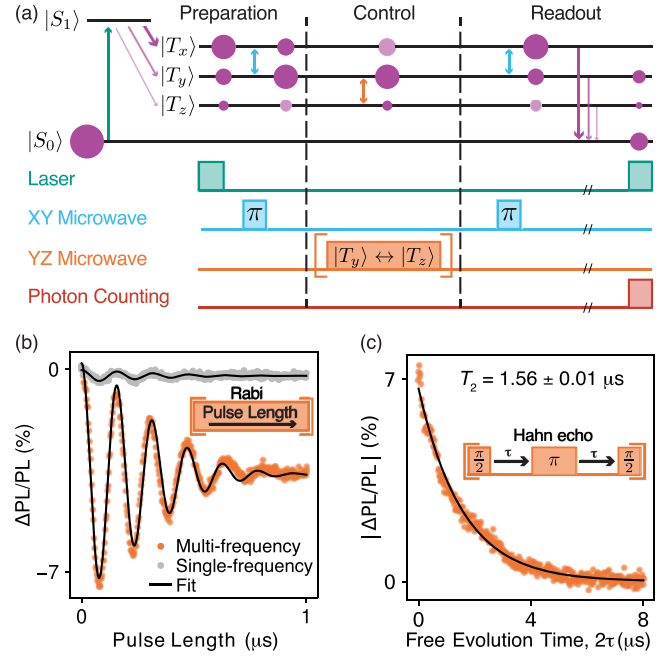


FIG. 4. Multifrequency driving. (a) Pulse sequence. A π pulse on the $|T_x\rangle \leftrightarrow |T_y\rangle$ transition increases the spin polarization between $|T_y\rangle \leftrightarrow |T_z\rangle$. A second microwave frequency controls the $|T_y\rangle \leftrightarrow |T_z\rangle$ transition, before population is transferred back to $|T_x\rangle$ through a final π pulse for more effective optical readout. (b) Rabi oscillations on the $|T_y\rangle \leftrightarrow |T_z\rangle$ transition measured with (orange) and without (gray) multifrequency control. (c) Hahn echo measured with multifrequency control. Fits are shown with black lines.

relevant physical quantity, which, as we discuss below, depends on a combination of coherence, optical contrast, spin concentration, and overhead times (rather than any one of these individually). Pentacene has a nonzero transverse zero-field splitting (i.e., E parameter), making it first-order insensitive to magnetic fields near zero field. While multiple quantum sensing modalities are possible [6–8,52] (including with a finite E parameter at zero field) as a quantitative illustrative example, here we benchmark magnetic-field sensitivities assuming a linear Zeeman splitting. Such behavior could be realized near zero field with related molecules having $E \simeq 0$, e.g., by using functionalized acenes [53] or molecules with threefold (or greater) symmetry [54,55]. Alternatively, a suitable field bias could be applied to optimize sensing in the high-field regime (see Supplemental Material for further discussion [29]). For ensemble-based sensing, the relevant metric is the volume-normalized sensitivity η^V [1,56]. (This quantity, equal to $\eta\sqrt{V}$, where η is the bare sensitivity and V the collection volume, is independent of the collection volume and therefore allows direct comparison between experiments probing different volumes of spins.) Taking $T_2 = 1$ μ s (which has been exceeded in the linear-Zeeman regime for pentacene [14])

and $T_2^* = 70$ ns (from spin-resonance linewidths in the linear-Zeeman regime for deuterated pentacene [34]), pentacene doping concentration $c_S = 0.1\%$, measurement overhead time $t_{\text{overhead}} \simeq 350$ μs (which accounts for initialization, readout, and reset), optical spin contrast $C = 0.075$, and an estimated average number of photons per molecule per readout of $n_{\text{av}} = 10^{-3}$ (reflecting imperfect photon collection efficiencies [1]), we calculate a volume-normalized sensitivity to ac fields of $\eta_{\text{ac}}^V \simeq 100$ $\text{nT}\mu\text{m}^{3/2}\text{Hz}^{-1/2}$ and to dc fields of $\eta_{\text{dc}}^V \simeq 1$ $\mu\text{T}\mu\text{m}^{3/2}\text{Hz}^{-1/2}$ (see Supplemental Material [29] for further details). Since the sensitivity scales (approximately) as $\eta^V \propto \sqrt{t_{\text{overhead}}}/(CT_2^* \sqrt{n_{\text{av}} c_S})$ [35], where T_2^* is T_2 (or the equivalent under dynamical decoupling) for ac sensing and T_2^* for dc sensing, there are multiple opportunities to improve these metrics. For example, the optical contrast can be improved by higher optical pumping rates, tuning depopulation rates, or reducing spin-lattice relaxation; coherence times can be improved through advanced control techniques [57]; overhead times can be reduced through engineering faster depopulation rates [36] and microwave-enhanced triplet depletion; and n_{av} improved through enhanced photon collection efficiencies [58] and tuning intersystem crossing rates [29]. Projecting that $C = 0.3$, $c_S \simeq 0.1\%$, $T_2^* = 100$ ns [37], $T_2 = 4$ μs [14], $t_{\text{overhead}} \simeq 35$ μs , $n_{\text{av}} = 0.01$ [5,58] could be achieved with future optimizations, we find volume-normalized sensitivities of $\eta_{\text{ac}}^V \simeq 1$ $\text{nT}\mu\text{m}^{3/2}\text{Hz}^{-1/2}$ and $\eta_{\text{dc}}^V \simeq 20$ $\text{nT}\mu\text{m}^{3/2}\text{Hz}^{-1/2}$ (see Supplemental Material for further discussion [29]). These values are promising given the state of the art for solid-state defects: $\eta_{\text{ac}}^V = 13$ $\text{nT}\mu\text{m}^{3/2}\text{Hz}^{-1/2}$ [5,56] and $\eta_{\text{dc}}^V = 34$ $\text{nT}\mu\text{m}^{3/2}\text{Hz}^{-1/2}$ [59]. Importantly, as highlighted above, sensing signal-to-noise ratios depend not only on the sensitivity, but also on minimizing sensor-target proximity [60], for which molecules are promising [61]: e.g., reducing sensor-target distances from $\simeq 10$ nm (representative of near-surface defects [62]) to $\simeq 2$ nm (corresponding to few-monolayer pentacene [63]) would result in a 100-fold increase in magnetic-dipole coupling.

Conclusion and outlook—Our Letter demonstrates that the key function of room-temperature optically detected coherent spin control can be realized in molecular systems, and we anticipate this can be extended to a range of molecules. Such behavior opens opportunities such as high density ensemble-based sensing with orders of magnitude higher active spin concentrations than in defect systems, where undesired defect creation is a limitation. (For example, the microsecond coherence times we measure are comparable to NV-center samples with ~ 10 ppm NV-center concentrations [56].) The versatile deposition techniques available to organic chromophores could be used to maintain proximity between sensor and target, even on textured or flexible surfaces, for applications such as

wide-field spin-based imaging with high spatial resolution [64]. By harnessing chemical tunability, coupling to other physical quantities, such as electric fields [65], could be optimized. The bright optical transitions (~ 10 ns fluorescence lifetime) of organic chromophores such as pentacene, combined with our demonstration of contrasts exceeding 15%, indicates promise for room-temperature optically detected coherent manipulation of individual chromophores. Additionally, organic triplets offer a complementary approach to interfacing nuclear spin memories under ambient conditions [66], combining optically readable metastable states with deterministic placement of nuclear spins via synthetic chemistry [26,67]. Extending our results to functionalizable molecules could enable the high sensitivity of optical detection to be combined with recently developed spin-labeling techniques [21–23] for structural analysis of individual biomolecules [68], and to realize spin-enhanced molecular labels for ultrasensitive fluorescent assays [69], or contrast agents for biomedical imaging in scattering media [70]. Overall, our results establish the key functionality for spin-based molecular quantum sensors at room temperature, paving the way for the application of such systems across disciplines.

Note added—Recently, we became aware of Ref. [71] with complementary results.

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Data availability—The data underlying this work are available at [72].

A. M., S. K. M., and A. C.-S. performed ODMR measurements. A. M., S. K. M., A. C.-S., and S. L. B. analyzed the ODMR data. M. A. prepared and characterized the crystal samples. M. A. and E. B. prepared and characterized the film samples. S. H., D. R. M., M. A., and S. L. B. provided oversight and supervision. A. M., S. K. M., A. C.-S., and S. L. B. wrote the manuscript with input from all authors.

The authors declare no competing interests.

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