Move Aside Pentacene: Diazapentacene-Doped para-Terphenyl, a Zero-Field Room-Temperature Maser with Strong Coupling for Cavity Quantum Electrodynamics

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Masers can deliver ultralow-noise amplification of microwave signals in medical imaging and deep-space communication, with recent research being rekindled through the discovery of gain media operating at room-temperature, eschewing bulky cryogenics that hindered their use. This work shows the discovery of 6,13-diazapentacene doped in para-terphenyl (DAP:PTP) as a maser gain medium that can operate at room-temperature, without an external magnetic field. With a maser output power of $-10$ dBm, it is on par with pentacene-doped para-terphenyl in masing power, while possessing compelling advantages such as faster amplification startup times, being pumped by longer wavelength light at 620 nm and greater chemical stability from nitrogen groups. Furthermore, the maser bursts from DAP:PTP allow one to reach the strong coupling regime for cavity quantum electrodynamics, with a high cooperativity of 182. The optical and microwave spin dynamics of DAP:PTP are studied in order to evaluate its capabilities as a maser gain medium, where it features fast intersystem crossing and an advantageously higher triplet quantum yield. The results pave the way for the future discovery of similar maser materials and help designate them as promising candidates for quantum sensors, optoelectronic devices and the study of cavity quantum electrodynamic effects at room-temperature.

1. Introduction

Accessing the strong-coupling regime of cavity quantum electrodynamics (cQED) in a benchtop system operating at room-temperature represents an alluring engineering goal. A high quality-factor ($Q$) microwave resonator magnetically loaded with optically pumped pentacene doped in para-terphenyl (Pc:PTP) provides one route toward this goal,[1] and diamond with negatively charged nitrogen-vacancy defects (NV$^-$ diamond) has also been considered.[2] However, attaining a sufficiently high spin polarization density for strong coupling from other materials has, at room-temperature, proven elusive.

Room-temperature masers (microwave amplification by stimulated emission of radiation) can be made out of either Pc:PTP or NV$^-$ diamond,[4,5] but Pc:PTP remains the sole material able to maser without any externally applied magnetic field (zero-field) at room-temperature. Unfortunately, it has a drawback in that it suffers from lag (of several microseconds) at start up; when operating in pulsed mode (e.g., providing low-noise amplification solely when required) this lag excludes applications that require a rapid response. Since masers on the benchtop remain as tantalizing prospects for achieving ultralow-noise amplification applicable to MRI in medical devices, deep space communication and for demonstrating cQED at room-temperature,[3] the discovery of other maser materials could help accelerate developments in these fields.

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DOI: 10.1002/adma.202300441
Previous literature had investigated the electronic structures and spin dynamics of various molecular alternatives to Pc:PTP as masers.[3] A particularly promising candidate was 6,13-diazapentacene doped in para-terphenyl (DAP:PTP), which was postulated to mase through a population inversion between its photoexcited triplet sublevels, \( T_x \) and \( T_z \).[4] However, no attempt was made to make a maser out of it or characterize the spin dynamics of its triplet state. In this work, we report on the successful masing of DAP:PTP on its \( T_x-T_z \) transition near 1478 MHz, as only the second gain material discovered that can do so at both zero-field and room-temperature. The steady-state and transient optical absorption properties of DAP:PTP were characterized alongside its triplet state dynamics using zero-field transient electron paramagnetic resonance (ZF-trEPR). The experimental masing signals were then measured, which showcased Rabi oscillations that were simulated to show the high cooperativity of DAP:PTP in the strong coupling regime. This all highlights DAP:PTP as an advantageous material for not only masers but also the exploration of cQED at room-temperature.

2. Results

2.1. Optical Characterization

DAP:PTP has a population inversion between the \( T_x \) and \( T_z \) sublevels,[3] and the ratio in which these sublevels are populated depends on optical pumping from a singlet ground state \( (S_0) \) to a singlet excited state \( (S_1) \), followed by intersystem crossing (ISC) that selectively populates the sublevels differently. A simplified Jablonski diagram in Figure 1a illustrates this process (alongside a depiction of a DAP:PTP lattice in Figure 1b), and so the optical properties of singlet excitation rates, ISC and depopulation away from the triplet states all play a vital role in the masing capabilities of DAP:PTP. To begin interrogating the optical properties of DAP:PTP, we initially compared its steady-state visible optical properties to Pc:PTP. DAP:PTP exhibits a UV/vis absorption spectrum and fluorescence output redshifted by \( \approx 30 \) nm compared to Pc:PTP with characteristic Frank–Condon vibronic bands and \( \lambda_{\text{max}} = 620 \) nm (Figure 2a). The ability to pump maser gain media at lower optical frequencies enhances their potential efficiency, since the number of absorbed photons per unit of pump energy increases. Since the majority of absorbed pump energy is lost internally through vibrational relaxation and heating, reducing the pump energy also minimizes the risk of charring the gain material.

The transient excited state dynamics of DAP:PTP following photoexcitation are also important for judging its merit as a maser. We performed time-correlated single photon counting (TCSPC) spectroscopy on single crystal shards grown within \( 4 \times 0.6 \) mm rectangular capillary tubes. To achieve sufficient signal-to-noise for the measurement, a higher-than-saturation concentration of 0.05% DAP:PTP was achieved using a relatively rapid crystal growth rate of 10 mm h\(^{-1}\). However, this resulted in significantly smaller individual crystal domains than samples grown at a slower rate (4 mm h\(^{-1}\) growth) for maser experiments.

The fluorescence lifetime (\( \tau_f \)) of DAP:PTP was found to decay biexponentially, with a monoexponential fitting function unable to describe the earliest time points and a triexponential decay offering negligible improvement to the fitting (Figure 2b). This analysis returned a relatively short lived decay lifetime of \( \approx 0.46 \) ns \( (A = 0.96) \) alongside a longer lifetime of \( 3.7 \) ns. By comparison, the \( \tau_f \) of Pc:PTP is known to be \( \approx 9 \) ns at room-temperature.[6] This confirms that despite being based on the same molecular scaffold, the nitrogen substitution on 6,13-diazapentacene (DAP) results in significantly faster excited state dynamics. The necessity for a biexponential fitting suggests two dominant decay mechanisms from \( S_1 \). Typical relaxation routes for dilute solutions, films or crystals of linear acenes include fluorescence and non-radiative decay, the latter of which can consist of vibrational decay from \( S_1 \) to \( S_0 \) or ISC into the triplet manifold. At 0.05% doping concentration, alternative decay mechanisms such as triplet-triplet annihilation are not expected to contribute significantly. DAP and pentacene (Pc) are similar in structure and extent of electron delocalization, so their transition dipole moments and resulting rates of

![Figure 1](https://www.advmat.de/wissenschaftlichePublikationen/2023/35/2300441/2300441-2of11.png)

Figure 1. a) Simplified Jablonski diagram showing optical pumping of DAP:PTP using 620 nm light to the singlet excited state. The population of spins then transfer to the triplet sublevels (each labelled according to the molecular axes drawn on a DAP molecule) through intersystem crossing, where the frequency of the transition between \( T_x \) and \( T_z \) is shown and the sublevel population ratios are given.[8] The populations then decay back to the singlet ground state through depopulating rates labelled as \( k_i \), where \( i = x, y, z \) refers to different depopulating rates for each sublevel. b) Drawing of a DAP molecule (green) doped into a unit cell of a PTP lattice (gray), where the DAP substitutes out one of the PTP molecules.
fluorescent relaxation are likely to be similar. Therefore, the reduced fluorescence lifetime of DAP:PTP compared to Pc:PTP indicates a faster rate of ISC.

To further assess the decay of $S_1$, visible and near-infrared (NIR) femtosecond transient absorption spectroscopy (fsTAS) was utilized to search for signature singlet and triplet state absorption bands. Measurements were conducted up to 5.9 ns, thereby covering the majority of $S_1$ decay as indicated by TCSPC spectroscopy. The TAS spectrum of DAP:PTP exhibited a negative ground state bleach (GSB) at 531 and 572 nm, corresponding to Frank–Condon absorption bands in the steady-state visible spectrum (Figure 2c). The broad positive bands to ESA transitions between $T_1$ and $T_2$ states. Global analysis by singular value decomposition (SVD) of these spectra revealed two significant principal components for both visible and NIR regions represent the total depletion of $S_1$ states. Since these components are a function of the abundance of $S_n$ states, their decay is intrinsically linked to both fluorescence and non-radiative decay, that is, internal conversion (IC) and ISC. However, triplet absorption is not, hence the time constant of 685 ns derived from the second component in the NIR region can be associated with the rate of ISC ($\kappa_{\text{ISC}} = 1/\tau_{\text{ISC}}$), yielding a rate of $1.46 \text{ ns}^{-1}$. This is consistent with the earlier assertion that the in-growing GSB features, which exhibit a very similar 641 ps lifetime, are linked with an increase in the presence of the triplet state. Since the total rate of fluorescence ($\kappa_f = 1/\tau_f = 2.174 \text{ ns}^{-1}$) is the sum of the rates of radiative decay ($\kappa_{\text{rad}}$), IC ($\kappa_{\text{IC}}$) and ISC ($\kappa_{\text{ISC}}$), it can be determined that $\kappa_{\text{ISC}} + \kappa_{\text{rad}} = 0.714 \text{ ns}^{-1}$. Having quantified $\kappa_f$ and $\kappa_{\text{ISC}}$, the triplet quantum yield ($\phi_T$) can be estimated as their ratio, yielding $\phi_T = 67\%$, higher than the accepted $\phi_T = 62.5\%$ for Pc:PTP.

The transient excited state spectrum of Pc:PTP exhibits many similar features to that of DAP:PTP, with a negative GSB at 508 and 546 nm, a broad ESA superimposed throughout the observable spectrum and additional negative bands at 600 and 644 nm matching the steady-state fluorescence spectrum (Figure 2d). A clear difference compared to DAP:PTP is that the decay of these features extends beyond the 5.9 ns termination of the measurement. Furthermore, our measurements and subsequent analysis by SVD were unable to discern any bands that could sensibly be associated with the triplet state other than the in-growing GSB (see Supporting Information). In this instance, while two components were required to sufficiently account for the visible spectrum, only one component was found to harbour a significant weighting for a description of the NIR region.

All components return monoexponential decay rates between
4.5 and 10 ns. Here, the first component of the visible region represents the only in-growing component. Therefore, similar to DAP:PTP, this likely represents a growing abundance of T1 states and the associated 7 ns lifetime can be approximated as τISC (giving κISC = 0.143 ns⁻¹). However, the observed spectrum only represents a partial relaxation of S1 states, so this is likely an underestimation. In the literature, τ for room-temperature Pc:PTP is given as a value between 8–10 ns, which is closely matched by the 10 ns lifetime of the second visible component.⁶,¹⁰,¹ⁱ Therefore, we expect τISC to be longer than 8 ns.¹² The search for triplet state absorptions for Pc:PTP would then require nsTAS measurements, which were beyond the scope of this work. We note that within the frame time of the experiment, the spectra of both Pc:PTP and DAP:PTP were devoid of triplet absorptions at 520 and 510 nm, respectively, which were previously used by Kouno et al., 2019 to determine the triplet lifetimes.¹³ Together, these data comprehensively demonstrate that the triplet quantum yield is markedly higher for DAP:PTP than Pc:PTP, which is a favourable attribute for achieving a higher amount of spins and hence a higher gain in maser devices.

2.2. Density Functional Theory Calculations

To understand how the chemical structures of Pc and DAP might relate to their observed optical properties, we conducted time-dependent density functional theory (TD-DFT) quantum calculations to observe the singlet and triplet states. Prior to excited state calculations, each molecule was optimized to find their respective singlet and triplet geometries using a polarizable continuum model (PCM) of benzene to approximate the non-polar environment of para-terphenyl (PTP)⁴. To provide a more intuitive depiction of the states relative to each other, the calculated energies were normalized against the energy of the ground state, such that the energy of S0 = 0 eV. The energy of each successive state is then given by their calculated excitation energy. Using this approach, the experimental trends were reproduced with the S0 to S1 excitation energy of DAP red-shifted by 30 nm (0.2 eV) compared to Pc (see the expanded Jablonski diagram in Figure 3a), while the absolute excitation energies are underestimated by ~15%, which is typical of TD-DFT calculations. The energy gap between S1 and T2 (ΔEST) can be estimated as 0.12 eV for DAP, compared with 0.27 eV for Pc. Since unfunctionalized linear aromatic hydrocarbons only exhibit weak spin–orbit coupling,¹⁴,¹⁵ ΔEST is closely linked to κISC following Fermi's golden rule.¹⁶ Thus, even small differences in ΔEST can have profound impacts on κISC and φT. For example, κISC has been shown to differ by two orders of magnitude as a result of a 20 meV difference in ΔEST between alternative Pc lattice sites in a PTP crystal host.¹⁷ While TD-DFT-based estimations of excited state energies are useful for understanding the relative ΔEST of different Pc derivatives, ab initio calculations of DAP and Pc comparing the use of a PCM to an explicit host model have demonstrated that the latter is required to properly account for the influence of the host.¹⁸ Hence, due to additional weak charge transfer interactions between DAP and PTP described by Charlton et al., our estimated ΔEST likely represents a small overestimation.¹⁸

Since spin–orbit coupling in organic molecules is mainly derived from transitions involving non-bonding orbitals, we considered if the 6,13-position nitrogen atoms may influence κISC through incorporation of their lone pair p-orbitals. TD-DFT calculations of DAP and Pc reveal that the transition between S0 and S1 only involves the HOMO and LUMO. An analysis of the natural transition orbitals for DAP indicate very similar π–π* character devoid of out-of-plane non-bonding contributions, similar to Pc. Hence, according to the El-Sayed approximation where κISC depends on a change in orbital type,¹⁶,¹⁹ the nitrogen substitution at the 6,13-positions is not expected to contribute significantly to the formation of triplets. Indeed, further calculations indicate that DAP exhibits only a weak degree of spin–orbit coupling between singlet and triplet states, particularly between S1 and T1 states (refer to Table S1, Supporting Information). Overall then, it is expected that the increased κISC observed for DAP relative to Pc is principally due to the reduced ΔEST.

2.3. Zero-Field Transient EPR

Before attempting to laser DAP:PTP on its T1–T2 transition, the transition frequency was found using ZF-trEPR when the sample was excited by a 620nm laser pulse. The strongest

![Figure 3](https://via.placeholder.com/150)

**Figure 3.** a) Expanded Jablonski diagram for Pc and DAP constructed with TD-DFT-derived energies for the excited electronic states of singlet and triplet optimized geometries. b) Calculated HOMO and LUMO orbitals of DAP and Pc.
The voltages of the ZF-trEPR signals are then proportional to the population difference between $T_x$ and $T_z$, denoted as $N_x(t) - N_z(t)$. The time evolution of $N_x$ and $N_z$ can be represented by a group of differential equations

$$
\begin{bmatrix}
N_x(t) \\
N_z(t)
\end{bmatrix} =
\begin{bmatrix}
-w_{xz} - k_x & w_{zx} \\
w_{zx} & -w_{xz} - k_z
\end{bmatrix}
\begin{bmatrix}
N_x(t) \\
N_z(t)
\end{bmatrix}
$$

(1)

where $w_{xz}$ is the spin–lattice relaxation rate between $T_x$ and $T_z$, $k_x$ and $k_z$ are the depopulation rates of these two sublevels.\(^{[20]}\)

The upward and downward spin–lattice relaxation rates are assumed to be the same at room-temperature since they are related by the Boltzmann factor.\(^{[21]}\)

The signal at 1478 MHz was rescaled such that the maximum amplitude was 0.41 (Figure 4a), corresponding to the maximum population difference (i.e., $N_x(0) - N_z(0) = 0.41$ with $N_x(0) + N_z(0) + 1$) between those two sublevels.\(^{[19]}\) A biexponential fitting was then applied to the signal as in Equation 2, in order to find the relaxation rates:

$$
N_x(t) - N_z(t) = A \exp(\alpha t) + B \exp(\beta t)
$$

(2)

$$
\alpha = -(w_{xz} + k_{xy}) + \sqrt{w_{xz}^2 + (\Delta k)^2}
$$

(3)

where $\alpha$ and $\beta$ are two eigenvalues of the coefficient matrix in Equation 1. $k_{xy} = (k_x + k_z)/2$ and $\Delta k = (k_x - k_z)/2$. The simulated curve is shown as the green curve in Figure 4a, with the fitted parameters being $A = 0.547 \pm 0.003$, $B = -0.066 \pm 0.005$, $\alpha = (-3.93 \pm 0.06) \times 10^3 \text{s}^{-1}$ and $\beta = (-0.459 \pm 0.017) \times 10^3 \text{s}^{-1}$.

According to Equation 3, the combination of two depopulation rates can be calculated as

$$
w_{xz} + \frac{k_x + k_z}{2} = -\frac{1}{2}(\alpha + \beta)
$$

(4)

which corresponds to a decay rate of $0.2 \times 10^6 \text{s}^{-1}$ (decay time 4.6 µs). This gives an upper limit on the decay time of the spins, as it is not possible to separate the spin–lattice relaxation rate and depopulating rates from this simulation without knowing them independently.

### 2.4. Maser and cQED Experiments

In order to reduce the applied optical pump energy required to mase, a microwave cavity with a high loaded quality factor ($Q_L$) and low mode volume ($V_m$) was constructed in order to boost the spin–photon coupling strength via the Purcell effect.\(^{[22]}\)

Figure 5a shows the cavity consisting of an outer copper cavity enclosing the transparent strontium titanate (STO) dielectric ring resonator. The TE$_{015}$ mode of the STO resonator resonated at $f_{\text{mode}} = 1478 \text{ MHz}$, which could be tuned by raising/lowering the ceiling of the copper cavity via turning a screw.

The DAP:PTP single crystal was then placed in the STO ring and pumped with a 5 ns laser pulse at 620 nm, with a repetition rate of 10 Hz and average energy of 13.5 mJ per pulse. Using a coupling wire loop attached to a coaxial cable, the maser output was coupled out from the cavity and passed through an isolator and bandpass filter before detection. The power envelope of a
single shot of the maser burst is shown in Figure 5b, lasting for ~10 µs (laser trigger at 0 µs). The cavity was tuned to a frequency $f_{\text{mode}}$ that maximized the maser output, which was found to be $1474 \pm 1$ MHz. The frequency was measured using a vector network analyzer (VNA) to read the $S_{11}$ reflection dip of the cavity at the frequency of maximum maser output, with an estimated error of 1 MHz due to the frequency span of the VNA limiting precision. The difference between the masing signal frequency and the ZF-trEPR frequency ($1478 \pm 2$ MHz) is likely due to slight heating of DAP:PTP from constant laser excitation in an enclosed insulating cavity, which lowered the resonant frequency. The maser burst features Rabi oscillations due to the strong coupling between the DAP:PTP spins and the microwave photons of the electromagnetic mode, and have a measured Rabi frequency of 1.6 MHz.

Figure 5c shows the comparison between maser bursts using different pump wavelengths (with identical pulse energy and repetition rates) at 570 nm (corresponding to an absorption peak in Figure 2a) and 532 nm, the wavelength of frequency-doubled Nd:YAG lasers. Since 620 nm was the wavelength of highest peak absorption in Figure 2a and lower wavelengths featured lower absorption peaks, the maser power output correspondingly decreases at shorter wavelengths for DAP:PTP due to lower absorption of the pump power (i.e., fewer triplet spins generated). However, all pump wavelengths still give substantial maser powers at ~12 dBm for 570 nm excitation and ~21 dBm for 532 nm excitation. The maser bursts also reach peak powers at later times for shorter wavelengths of laser excitation; 1.5 µs for 620 nm excitation and 3 µs for 532 nm excitation.

Figure 6a compares the maser outputs between DAP:PTP and Pc:PTP. The cavity setup, $Q_{\text{c}}$, and measuring apparatus were identical as in Figure 5a, except for how both crystals were excited with 532 nm pulsed light with an average energy of 7 mJ per pulse, and the cavity was tuned near 1450 MHz for the Pc:PTP maser output. The trigger time of the laser in Figure 6a is the same between the two materials, hence DAP:PTP is seen to reach its peak maser power faster than Pc:PTP. The maser output of Pc:PTP however lasts slightly longer than that of DAP:PTP; 12 µs for the former compared to 8 µs for the latter. This may be due to the faster spin–lattice relaxation and/or depopulating rates in DAP:PTP, which is evident from its shorter ZF-trEPR signal in Figure 4 compared to that of Pc:PTP, which lasts for about 40 µs. Additionally, the presence of the nuclear spins of nitrogen resulting in additional spin–spin interactions may lead to faster spin dephasing in DAP:PTP and thus also contribute to the shorter maser duration. Finally, both preserve Rabi oscillations for the duration of the maser burst.

When not constrained to using the same pumping wavelength, Figure 6b shows the highest peak maser powers of DAP:PTP and the only two other known room-temperature masers when pumped with their ideal wavelengths. Pc:PTP still has the highest reported peak power (~6.8 dBm) when pumped with 592 nm light, but DAP:PTP is quite close at ~10 dBm when pumped with 620 nm light. Importantly, DAP:PTP can achieve this peak power with less than half the $Q_{\text{c}}$ used in the Pc:PTP masing experiment in previous literature (3690 for the former versus 8500 for the latter) and slightly less pump energy (13.5 mJ for DAP:PTP versus 15 mJ for Pc:PTP), which denotes a lower masing threshold for DAP:PTP when pumped with 620 nm light.

This possibility was explored through measuring the threshold laser pump pulse energy that was able to produce a masing signal from DAP:PTP, which was found to be 2.3 mJ (see Supporting Information). Besides pulse energy, the Purcell factor of a maser cavity should be taken into account for a fair comparison of maser thresholds. The Purcell factor is directly proportional to $Q_{\text{c}}$ divided by the mode volume ($V_{\text{m}}$) of the cavity ($Q_{\text{c}}/V_{\text{m}}$), and the higher it is, the easier it
is to mase (overcome threshold). The mode volume is further explained in Supporting Information. Previous work had measured the threshold laser pump pulse energy of Pc:PTP, with its ideal pumping wavelength of 590 nm, to be 4 mJ.\[^{[25]}\] The Purcell factor of their cavity was proportional to 4900/(0.4 cm\(^3\)) = 12 250 cm\(^{-3}\). For the cavity in this work, the mode volume was calculated using the finite-element method in COMSOL to be 0.32 cm\(^3\). Hence, our Purcell factor was 3690/(0.32 cm\(^3\)) = 11 531 cm\(^{-3}\). We also note how the reported concentration of the Pc:PTP crystal in the previous work is the same as our DAP:PTP crystal (0.01%). Hence, we believe that DAP:PTP has a lower maser threshold than Pc:PTP since it has a lower laser pump pulse energy threshold while also masing with a lower Purcell factor than in the Pc:PTP threshold experiments.\[^{[25]}\] Both Pc:PTP and DAP:PTP feature powers much higher than that reported for NV\(^{-}\) diamond, whose highest reported power was \(-90\) dBm\[^{[9]}\] under continuous operation. Finally, it is noted that the masing bursts for DAP:PTP and Pc:PTP are able to follow the repetition rate of the pump laser, and hence the masing signals seen in Figures 5 and 6 have a repetition rate of 10 Hz which follows the pumping repetition rate.

We now explore whether the masing of DAP:PTP in the microwave cavity has managed to reach the strong coupling regime vital for cQED experiments. The strong coupling regime can be reached when the ensemble spin–photon coupling (\(g_e\)) of a system greatly exceeds the cavity decay (\(\kappa_c\)) and spin-dephasing (\(\kappa_s\)) rates. This can be summarized by the “cooperativity” of the system defined as \(C = 4g_e^2/(\kappa_s\kappa_c)\).\[^{[1]}\] where strong coupling is reached if \(C \gg 1\). \(\kappa_c\) can be calculated to be \(2\hbar \Omega_{\text{mode}} Q_i \approx 2\pi \times 0.4\) MHz from the cavity setup, while the other two parameters \(\kappa_s\) and \(g_e\) can be estimated by simulating the maser burst in Figure 5b. This is done using a set of coupled differential equations derived from the master equation with a Tavis–Cummings Hamiltonian and the Liouvillian components accounting for the various decay pathways. These differential equations are the same as in previous literature\[^{[1]}\] for simulating the expectation values of the cavity photon number \(\langle a^\dag a \rangle\) (c), the spin–photon coherence \(\langle a^\dag S^- \rangle\) (its complex values) (d), inversion \(\langle S^+ \rangle\) (e), and spin–spin correlation \(\langle S^+ S^- \rangle/N(t)\) during the maser burst from DAP:PTP in Figure 5b are also shown here.

The maser burst can be converted to photon numbers through the following equation:

\[
\langle a^\dag a \rangle = P(t) \frac{1+K}{\hbar f_{\text{mode}} \kappa_c} \tag{5}
\]

where \(P(t)\) is the maser output power in units of watts and \(K\) is the cavity coupling coefficient (measured to be 0.20 using VNA methods.\[^{[26,27]}\] see Supporting Information). The coupled differential equations are solved so that they fit the observed \(\langle a^\dag a \rangle\) calculated from Figure 5b, in order to generate simulated expectation values in Figure 6c–f. The resulting parameters \(\kappa_{s, \text{sim}}\) and \(g_{e, \text{sim}}\) (denoted as such due to being simulated) were \(2\pi \times 0.29\) MHz and \(2\pi \times 2.3\) MHz respectively. This gives a cooperativity of \(C = 182\), which is about two orders of magnitude higher than that experimentally measured with collective NV\(^{-}\) spins,\[^{[28]}\] revealing the superiority of molecularly doped spin systems in terms of achieving strongly coupled spin–photon systems at ambient conditions.

We note however that there is a discrepancy between the simulated \(g_{e, \text{sim}}\) and its relation to the observed Rabi frequency (\(\Omega\)) of the maser burst. In previous studies of strongly coupled spin–photon systems, the ensemble spin–photon coupling strength \(g_e\) is equal to \(\Omega/2\).\[^{[29,30]}\] Based on this relationship and \(g_{e, \text{sim}} = 2\pi \times 2.3\) MHz, the Rabi frequency arising from the strong coupling between the spins and microwave photons

\[
\kappa_s \approx \kappa_c = 4g_e^2/(\kappa_s\kappa_c)\tag{6}
\]

\[
\kappa_s(\mu T) \approx 4g_e^2/(\kappa_s\kappa_c)\tag{7}
\]

In the previous work, it was calculated to be 2.3 MHz, the Rabi frequency arising from

\[
\kappa_s(\mu T) \approx 4g_e^2/(\kappa_s\kappa_c)\tag{7}
\]
in our experiment can be predicted to be $2\pi \times 4.6$ MHz. However, the Rabi frequency observed in our experiments was $\Omega = 2\pi \times 1.6$ MHz, which is almost three times slower than the predicted value. We attribute the discrepancy to the large number of excitations (i.e., microwave photons) in the cavity, $n_{\text{cavity}}$, arising from the masing process. It has been found that when $n_{\text{cavity}} \gg 1$ and comparable to the number of spins $N$, the Rabi frequency will be proportional to $\sqrt{n_{\text{cavity}}}$, which indicates the transition of the strong coupled spin–photon system from the quantum to the classical regime, where the photon can be treated as a classical field normally adopted in magnetic-resonance studies.

3. Conclusion

We have characterized the optical and zero-field spin dynamics of DAP:PTP, where it was shown to have an advantageously higher triplet quantum yield and faster $\kappa_{\text{ISC}}$ than Pc:PTP, alongside being able to absorb longer wavelengths of pump light. When operating as a maser and as a platform for room-temperature cQED, DAP:PTP was able to mase using three different pumping wavelengths: 532, 570, and 620 nm, the lattermost being its ideal pumping wavelength. Through this, we suspect that it can mase using any wavelength between 532 and 620 nm. When analyzed using the master equations, DAP:PTP gave a cooperativity of 182, which places it in the strong coupling regime for cQED at room-temperature. We found that DAP:PTP has compelling advantages against Pc:PTP: first, 620 nm light, which is most suitable to pump DAP:PTP, is easier to generate efficiently than shorter wavelength 590 nm light that is ideally used to pump Pc:PTP. Second, DAP:PTP has a faster masing startup time (less lag), and we believe it has a lower masing threshold which makes it easier to mase using less pumping power or lower $Q$. We hypothesize that this lower threshold may be related to the higher triplet quantum yield and faster ISC rate it possesses, which would translate to more spins per optical pulse being able to participate in masing. Third, DAP is also more chemically stable than Pc, since the presence of nitrogen groups makes it less air-sensitive. This would make doping it into PTp easier since it would not decompose as easily during crystal growth processes.

When compared head-to-head using pulsed 532 nm excitation (which is also the first time Pc:PTP has been reported to mase under 532 nm light), both materials perform almost equally well. DAP:PTP’s sole disadvantage would be its shorter spin–lattice relaxation time (shown by ZF-trEPR experiments) which causes its maser burst to decay faster than Pc:PTP under an identical excitation time, but it still maintains its faster startup time to reach peak amplitude. We believe the advantage of a faster startup time will outweigh the disadvantageous relaxation time since DAP:PTP could be used for microwave amplification of even faster signals than Pc:PTP, whereas the time of the maser signal could be lengthened by just using a longer optical pump pulse. Indeed, attaching a luminescent concentrator to DAP:PTP to attempt continuous-wave masing using longer pump pulses, as was performed with Pc:PTP, is a subject of future work, where its lower masing threshold may allow it to perform better. Indeed, we would be eager to send samples of DAP:PTP or Pc:PTP for experiments in masing to other research groups if requested, so as to proliferate research into room temperature masers.

In conclusion, DAP:PTP is a promising new room-temperature maser gain medium which can be excited with red (620 nm) light as well as green (532 nm) light, the latter being a common wavelength of workhorse frequency-doubled Nd:YAG pulsed lasers. As only the second material discovered to be able to mase at both zero-field and room-temperature in almost a decade, DAP:PTP can help further the search for other maser materials that share its properties, while acting as an attractive platform for studying room-temperature cQED with high cooperativity.

4. Experimental Section

Synthesis of DAP and DAP:PTP Crystal Growth: DAP was synthesized by co-melting 2,3-diaminophthalene (AlfaAesar, 97%) with napththalene-2,3-diol (Fluorochem, 95%) at 216 °C under argon for 1 h. The mixture was then cooled and formed into a slurry by vigorous stirring with acetone for 30 min. This solution was filtered to yield crude 6,13-dihydro-6,13-diazapentacene as brown powder which was heated in toluene under argon with chloranil (SigmaAldrich, ≥98%) for a further hour. The solution was filtered hot and washed with excess aqueous Na$_2$CO$_3$ to yield DAP as a dark green powder (80%). Prior to mixing with PTP, DAP was purified by vacuum sublimation at 220 °C. Dark green crystals formed after 2 days.

Samples of Pc:PTP and DAP:PTP were grown using the Bridgman method described previously. PTP (Sigma-Aldrich, ≥99.5%) was extensively purified by zone refining prior to use. DAP was mixed with PTP at 0.05% concentration by grinding in a pestle and mortar before being loaded into a 3.5 mm OD borosilicate NMR tube and sealed under argon. Bridgman growth was performed at 4 mm h$^{-1}$ over 3 days at 218 °C. Unlike Pc:PTP which grows as a homogeneous pink crystal, DAP:PTP grew as a banded crystal with a relatively clear section at the bottom, a homogeneous green section in the middle and a smaller concentrated section at the top. For maser experiments, the top and bottom bands were discarded and the concentration of the middle section was determined using UV/vis spectroscopy on samples of DAP in a clear glass of ortho-terphenyl at known concentrations. A calibration curve was constructed using absorbance at 614 nm, and the concentration was subsequently determined to be $0.01\%$ (Figure 7). All maser and ZF-trEPR experiments used DAP:PTP and/or Pc:PTP with 0.01% dopant concentration.

TCSPC: The time-resolved photoluminescence (PL) spectroscopy was measured with TCSPC which gave carrier recombination lifetimes of materials. A diode laser (NanoLED, HORIBA) was used to produce 1 mW cm$^{-2}$, <200 ps excitation pulses at a repetition rate of 1 MHz. 404 and 635 nm lasers were used as the excitation sources. A photomultiplier tube detector (PPD-900) collected photons at the desired wavelengths. The instrument response function was measured with a pristine sample substrate at the excitation wavelength. Additional long-pass filters were used before the detector to exclude scattering from the excitation source for some measurements.

Femtosecond Transient Absorption Spectroscopy: Measurements were collected using a broadband pump-probe commercial spectrometer (Helios, Spectra Physics, Newport Corp). Ultrafast laser pulses (800 nm, <100 fs pulse duration) were generated by a 1 kHz Ti:sapphire regenerative amplifier (Solstice, Spectra Physics, Newport Corp). The excitation pump and white light probe were converted from 800 nm pulses. The wavelength tunable pump light (400 nm in this work) was converted by an optical parametric amplifier (TOPAS Prime, Spectra-Physics) and a frequency mixer (Niruvis, Light Conversion). The white light probe was generated by another part of 800 nm pulses directed through a crystal (sapphire for the visible region and yttrium aluminium
of the focused probe and pump pulses were 0.5 mm² at the sample coupled multichannel spectrometers (CMOS sensors). The beam sizes changes between pump on and pump off were measured by fibre-optic with 500 Hz chopper. The time-resolved transmission spectrum delay between the pump and probe was controlled by a mechanical collinear optical path and overlapped at the sample position. The time is used as a reference.

Figure 7. UV/vis calibration curve used to estimate the concentration of the DAP:PTP maser crystal. Standard solutions were made using an ortho-terphenyl host. The concentration of the crystal used for maser experiments was estimated by diluting a representative piece of the DAP:PTP crystal with ortho-terphenyl until the sample adopted a transparent appearance as with the calibration standards.

To reduce the noise, the white light was split into two beams, where one is passed through the sample, and the other is used as a reference. Pump and probe light was focused on the sample with a non-collinear optical path and overlapped at the sample position. The time delay between the pump and probe was controlled by a mechanical delay stage with a time range of 6 ns. The pump light was modulated with 500 Hz chopper. The time-resolved transmission spectrum changes between pump on and pump off were measured by fibre-optic coupled multichannel spectrometers (CMOS sensors). The beam sizes of the focused probe and pump pulses were 0.5 mm² at the sample position. The pump light energies were measured with an energy meter (VEGA P/N 7Z01560, OPHIR Photonics). To reduce probe noise from laser fluctuation, the measured transmission spectrum difference was normalized to the reference probe spectrum and averaged for several scans to achieve a good signal-to-noise ratio. SVD analysis was performed using SurfaceExplorer (v4.3.0). Spectral and principal component data were then analyzed in OriginPro 2022b. Decay values were found by fitting a monoexponential decay function.

The signals were captured on an oscilloscope (Rigol DS1104 Z-plus) triggered by a photodiode (Thorlabs DET210). Each signal plot in Figure 4 is an average of 512 signals collected on the oscilloscope at a specific microwave frequency. In Figure 8, the microwave power was varied to study the relation between the EPR signal voltage and the input microwave power in order to avoid saturation. Once a suitably low enough microwave power was found to avoid saturation, which was −25 dBm (0.00316 mW), this power level was used for the experiments in Figure 4.

Maser Setup: The setup, pictured in Figure 9, consisted of the 0.01% DAP:PTP single crystal (cylinder-shaped, 4 mm diameter and 8 mm height) inserted into a microwave cavity, which was connected to a microwave isolator and bandpass filter before being connected to a logarithmic amplifier which acted as a detector.

The cavity consisted of a dielectric ring of a single crystal of strontium titanate (STO) housed within a cylindrical copper cavity. The STO ring (OD 12 mm, ID 4.05 mm and height 8.6 mm) was placed on a cross-linked polystyrene stand that raised it to 3 mm above the floor of the copper cavity. The copper cavity had an inner diameter of 30 mm and maximum inner height of 20.4 mm. An inductive loop, made by soldering a wire loop onto the end of an SMA connector coaxial cable (see photo in Figure 5), was inserted into the cavity to act as an output coupler for the maser burst. This coupling loop (called Port 1 in Figure 9) had a coupling coefficient of K ≈ 0.20 (undercoupled, refer to Supporting Information), and would have been coupled to the TE_{010} mode of the STO ring. The frequency of this mode could be adjusted by using a tuning screw to raise/lower the inner ceiling of the copper cavity. The Q₀ of the cavity was measured from Port 1 to be 3690 for all maser experiments in this work (with sample already placed inside). A second coupling loop (similar in make to the first and denoted as Port 2 in Figure 9) was also inserted into the cavity for monitoring the frequency using a VNA (HP8753A, lightly calibrated before measurements). This second coupling loop was severely undercoupled (K ≪ 0.20) to prevent reducing Q₀. When measuring and recording the maser signal, this second coupling port was left disconnected from everything.

Besides the main circular hole (5 mm diameter) used for allowing light to enter the cavity and pump the crystal from the side, the copper cavity featured slot gaps which were cut into its main body. These slot gaps (which were unrelated to masing experiments) were actually causing radiative loss for the microwave cavity which reduces...
could be calculated. The dataset was fitted to the equation (5), which finally gave the experimental plot in Figure 6c. The set of coupled differential equations that govern the evolution of $\langle a^\dagger a \rangle$, $\langle a^\dagger S^+ \rangle$, $\langle S^+ \rangle$ and $\langle S^- S^+ \rangle / N$ were solved using an explicit Runge–Kutta method of order 5(4) in Python (the default RK45 method of the “scipy.integrate.solve_ivp” solver), and by choice of proper parameters, the simulated plot of $\langle a^\dagger a \rangle$ was fitted to the experimental plot, after which the resultant parameters were used for simulating the other three expectation values. The differential equations, initial conditions used for the simulation and fitted parameters were all listed in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank Ben Gaskell of Gaskell Quartz Ltd. (London) for making the strontium titanate ring used. The authors also thank Dr. Ke-Jie Tan for growing DAP:PTP crystals many years ago, which helped when growing new DAP:PTP crystals for this work. The authors thank Professor Takeda Kazuyuki and Professor Yanai Nobuhiro for fruitful discussions on DAP:PTP and for lending samples for tests, as well as Dr. Artem Bakulin for helpful discussions on the optical properties. This work was supported by the U.K. Engineering and Physical Sciences Research Council through Grant No. EP/V048430/1, EP/W027542/1, and EP/V001914/1. H.W. acknowledges financial support from the National Science Foundation of China (NSFC) (Grant No. 12204040) and the China Postdoctoral Science Foundation (Grant No. Y20210035, No. 2021M700439).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
Keywords

electron spin resonance, masers, optoelectronics, quantum materials, spintronics, transient absorption spectroscopy

Received: January 14, 2023
Revised: March 4, 2023
Published online: April 9, 2023