

Phosphorescence detection as the first step toward all-optical spin manipulation in single perylene molecules

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The on-demand manipulation of triplet states in closed-shell single molecules is still out of reach due to a lack of information about the energy of those triplet states. Yet, the access to triplet states would open up a route toward an all-optical single-molecule photonic switch/transistor and, moreover, would provide a way of performing coherent spin operations from the spinless ground state. In this work, we take an important step toward those aims by measuring the triplet energy from the weak phosphorescence signal of perdeuterated perylene, embedded as a guest molecule in a dibenzothiophene host matrix, which well preserves the coherence properties of the perylene guest. We find that perylene's phosphorescence can be enhanced in this host matrix, when acting as an intermediary for the generation of triplet excitons. The triplet energy that we find can be used to significantly narrow down the search for the ultraweak spin-forbidden transitions from the ground singlet to the triplet states of a single molecule.

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I. INTRODUCTION

Spin-carrying systems provided by defects, such as nitrogen-vacancy (NV) centers in diamond [1], lanthanide ions in garnets [2], and the more recent discovered defects in hexagonal boron nitride [3], have emerged as powerful platforms for quantum applications. As these systems possess ground electronic states with nonzero spin multiplicity, direct access to spin levels is allowed. The microwave-induced spin transitions in such systems can be detected optically through changes in the defect's fluorescence signal, known as optically detected magnetic resonance (ODMR) spectroscopy. Beyond microwave-driven transitions, fully optical schemes—demonstrated in both NV centers [4] and atomic systems [5]—enable spin-state manipulation without the need for microwaves. Spin-photon interfaces, relying on light-matter coupling, could then be used to enhance control over the spin state [6].

The aforementioned spin systems have so far enabled a wide range of applications, including nanoscale magnetometry [7], thermometry [8], demonstrations of quantum entanglement [9], and the development of quantum memories [10] and of optomechanics [11]. While for quantum memories electron spins can enable efficient coherent transfer of quantum information to a nuclear spin network through hyperfine interactions, the inability to turn off the electron

spin after a write operation leaves a channel for decoherence for that memory [6]. In contrast, systems without spin in their electronic ground state—such as closed-shell aromatic molecules—naturally avoid this issue. For this reason, molecular crystals have also been proposed as a potential solution in levitated optomechanics, namely, in view of generating massive quantum states from a network of nuclear spins with long coherence times [12].

Typical aromatic molecules feature a singlet ground state, a singlet excited state, and an intermediate triplet excited state [see Fig. 1(a)] that can only be accessed by intersystem crossing from the singlet excited state. The triplet state comprises three spin sublevels (T_x , T_y , T_z), with their relative energies in zero magnetic field defined by zero-field splitting parameters D and E [13]. Following the discovery that particular single molecules embedded in host crystals can be detected by their fluorescence, magnetic resonance via ODMR was soon demonstrated for a pentacene molecule embedded in a *p*-terphenyl matrix [14,15]. Subsequent works have resolved hyperfine couplings to nearby nuclear spins, such as ^{13}C [16] and hydrogen [17]. While microwave-driven spin control is routine for single molecules, an all-optical counterpart—akin to those performed in NV centers and atomic systems—has yet to be achieved. With optical spin control, single-molecule fluorescence switches or transistors [18] could be realized [see working principle in Fig. 1(b)]. Moreover, in view of quantum memories, optical spin control would provide a direct path toward storing quantum information, without having to rely on stochastic intersystem crossing before such an operation can be applied.

Recent advances continue to stimulate research in the field of spin manipulations in molecules: Experiments, for example, include electron spin resonance of pentacene detected via atomic force microscopy [19], room-temperature ODMR of

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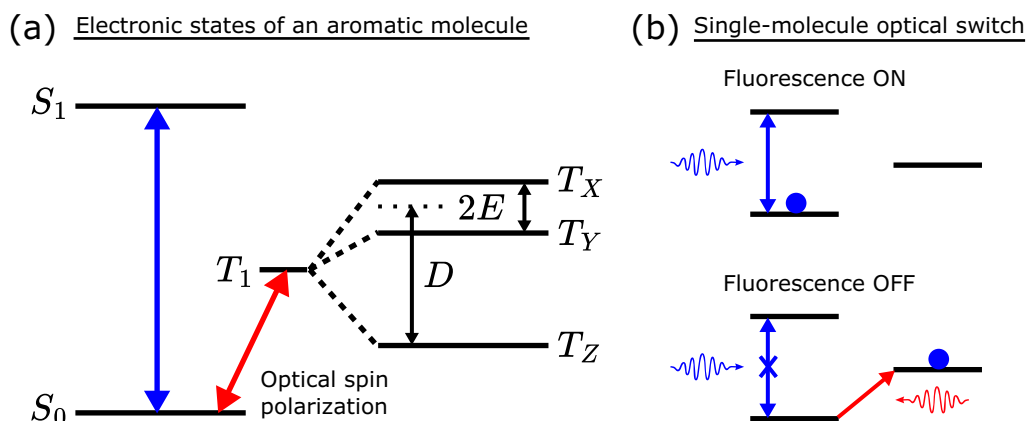


FIG. 1. The single-molecule optical switch. The energy level diagram of a typical closed-shell aromatic molecule has a simplified structure as shown in panel (a). Panel (b) shows that driving the transition from the ground state S_0 to the metastable T_1 state (red arrows) allows switching off the fluorescence cycles between S_0 and S_1 (blue arrows), explaining the switch/transistor action.

pentacene in *p*-terphenyl [20], spin manipulation in optically active organic radicals [21], and experiments on chemical species that have ODMR contrasts that well exceed those of NV centers [22].

To detect single molecules in an organic matrix, one requires a high fluorescence yield, which implies that the triplet yield should be as low as possible. However, to determine the energy of the triplet state, a high triplet yield is desirable. In this work, we build upon a recently developed host-guest system with low triplet yield [23], in which we detected single molecules with excellent photostability and spectral stability. The uniqueness of our approach lies in providing a work-around for this fundamental discrepancy: Rather than generating triplets via the guest molecules themselves, we exploit the host matrix to generate triplet excitons that subsequently transfer to the guest. By detection of the triplet energy of perylene, we have taken the first steps toward all-optical spin manipulation.

II. METHODS

A. Preparation of perylene- d_{12} molecules in a dibenzothiophene crystal

Perylene- d_{12} (Sigma-Aldrich, 98%) was dissolved in toluene (Acros Organics, 99.85%) to prepare millimolar concentration solutions. Dibenzothiophene (Sigma-Aldrich), previously purified by zone refining, was melted using a hot-air gun. The perylene solution was then pipetted into the molten dibenzothiophene. After a brief period of additional heating to fully evaporate the toluene, the mixture was rapidly cooled, causing it to solidify. A small amount of the resulting solid mixture was pressed between two glass slides and reheated. The thin liquid film formed between the slides was then rapidly frozen in liquid nitrogen to ensure uniform dispersion of perylene molecules within the dibenzothiophene crystals.

B. Measurement setup

The samples are measured in a liquid-helium flow cryostat (Janis, SVT-200-5) at a regulated temperature through control

of the flow of liquid helium and pressure. Measurements involving fluorescence [e.g., in Fig. 4(c)] were performed with a M-squared ECD-X laser. Measurements involving phosphorescence were performed with a 100 W electrical power mercury lamp, placed in a housing (Oriel 60028) that boosts the light collection efficiency from the lamp and collimates the output beam. The ultraviolet part of the mercury emission spectrum (see Fig. S1 in the Supplemental Material [24]) is transmitted by a filter (FSR-U340) and focused onto a feedback-controlled optical chopper wheel (Bentham 418F). The intensity-modulated light (UV optical power of approximately 2.5 mW) is then loosely focused (>5 mm beam waist) onto the sample. The emitted light from the sample is subsequently collected from another window of the cryostat and directed to the opposite side of the chopper wheel. This is to ensure that the time windows of excitation and emission are not overlapped, but delayed. The duration of the delay between the end of the excitation window and the start of the acquisition window is controlled by the chopper frequency. The emitted light is then focused onto the slit of the spectrometer (Horiba IHR-320) with an attached Symphony II CCD detector or to a single-photon counting module (Excelitas, SPCM-AQRH-16). For the single-molecule experiments, we made use of a home-built confocal setup with a sacher diode laser (Littman/Metcalf) as a tunable excitation source, allowing us to work in the wavelength range of 452–457 nm at a spectral linewidth of 100 kHz.

III. RESULTS AND DISCUSSION

Perylene guest molecules embedded in a dibenzothiophene host matrix constitute a host/guest system that exhibits narrow, highly stable spectral resonances at cryogenic temperatures, as demonstrated in our previous investigations of this material system [23]. The presence of such narrow and stable resonances—effectively free from spectral diffusion—enables the isolation of individual molecular resonances from within an inhomogeneously broadened ensemble (see the close-up in Fig. 2). This capability allows for prolonged measurements on single molecules, which is essential for obtaining stable fluorescence signals while searching for dark

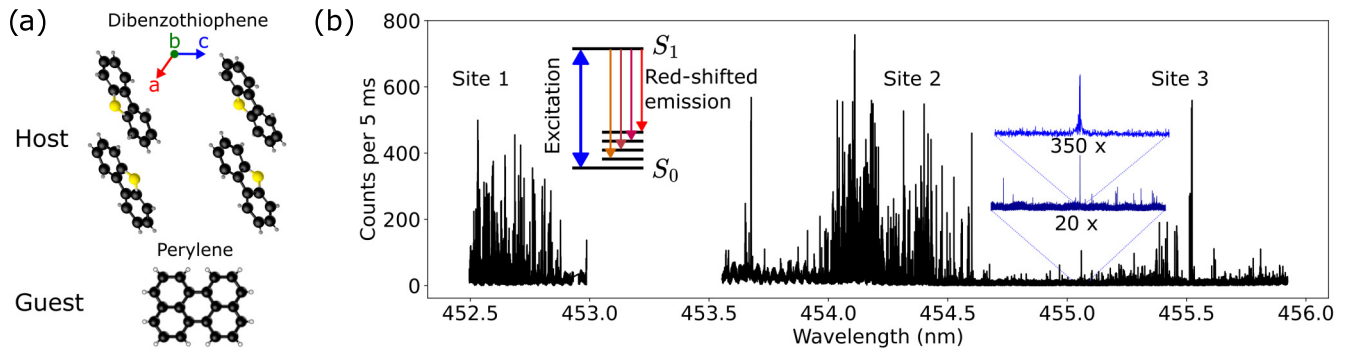


FIG. 2. Selecting single resonances from an inhomogeneous distribution. (a) The molecular system is built up by host crystals of dibenzothiophene ($P_{21/c}$ space group), doped with a concentration of perylene guest molecules according to the procedures noted in the “Methods” section. (b) Within a single crystal of dibenzothiophene, the resonances from single perylene molecules in a dibenzothiophene crystal are found to be scattered over a wide range of wavelengths and are observed by collecting the redshifted emission once the excitation laser hits resonance with a zero-phonon line. There are likely three distributions within the scanned range, where the part between 453 and 453.5 nm was skipped—a usually sparsely populated region for perylene resonances. The resolution of the scan is 6 MHz at an integration time of 5 ms per data point, making the total scan duration a minimum of 43 min—excluding times required to move the motor of the laser grating. Based on an excitation volume on the order of a few μm^3 , the concentration of perylene molecules is on the order of tens of nmol/mol.

transitions to the triplet state. Such transitions would manifest as changes in the fluorescence rate, analogous to the optical detection of microwave-induced transitions between triplet spin sublevels.

The inhomogeneous distribution of perylene molecules, as depicted in Fig. 2, indicates the presence of at least three distinct subdistributions among the >527 detected molecules. These clusters, commonly referred to as spectroscopic sites, likely arise from variations in the local environment as molecules are incorporated into the host matrix, while other sources of structural inhomogeneity, such as isotope effects, contribute only marginally to the observed energy shifts [16]. A detailed examination of a single resonance, magnified by a factor of 350, reveals a characteristic linewidth of less than approximately $\sim 10^{-5}$ nm (~ 100 MHz), approaching the natural, lifetime-limited linewidth of 45 MHz for this system [23]. This linewidth is over 5 orders of magnitude narrower than the full scan range (~ 5 THz). In contrast, if one would search for a dark optical resonance to the triplet state, it must be taken into account that typical spin transitions, such as revealed by ODMR, are with ~ 1 MHz even a factor $100\times$ narrower (narrowing further to ~ 0.1 MHz for perdeuterated molecules) [16]. During the whole scan, the perdeuterated must stay at resonance with the probe laser to keep a steady fluorescence signal, as a reference for when the other laser hits resonance with a dark transition to the triplet. Moreover, the integration time per pixel must be much longer than that in Fig. 2, as natural occurrences of intersystem crossing make the fluorescence signal fluctuate. With integration times much longer than the triplet lifetime ($\sim \text{ms}$), for example, 1 s, these fluctuations can be averaged out. A comparative scan for a triplet transition would thus take over 5 million seconds or two months.

The search for an ultranarrow transition to the triplet state is therefore a considerable challenge, akin to locating a needle in a haystack. This search can be substantially refined if the approximate triplet-state energy for the molecular ensemble is known. While several methods exist for detecting triplet-state signals, direct absorption techniques are rendered impractical

due to the extremely weak oscillator strengths associated with singlet-triplet transitions ($\sim 10^{-10}$). Additionally, the generally low intersystem crossing rates and poor phosphorescence quantum yields characteristic of typical fluorophores employed in single-molecule spectroscopy (a comprehensive list is provided by Adhikari *et al.* [25]) further complicate direct detection.

Perylene is a particularly attractive choice in this context, as it is among the bluest known single emitters, and according to the energy gap law, is predicted to possess a higher phosphorescence quantum yield. Notably, it remains the only molecule for which phosphorescence has been observed in cryogenic single-molecule spectroscopy experiments, namely, when embedded within an anthracene host matrix [26]. However, unlike perylene in dibenzothiophene, single-molecule detection was not achievable in that system, later attributed to intermolecular intersystem crossing effects [27]. While the triplet energy of perylene has been determined in anthracene ($12\,844\text{ cm}^{-1}$) and in pure crystalline form ($12\,372\text{ cm}^{-1}$), these values can only serve as approximate references for dibenzothiophene, as solvent-induced shifts can significantly alter the electronic energy levels of guest molecules across different host matrices.

The separation of the ultraweak phosphorescence signal from the much stronger fluorescence background can be achieved through time-gated detection. Given that the fluorescence lifetime of perylene is on the order of nanoseconds, while the triplet-state lifetimes extend into the millisecond regime [23], time-resolved measurements allow effective discrimination between these emission processes. However, the yield of excited triplets remains relatively low, with only approximately 1 in 10^6 excited singlet states undergoing intersystem crossing to the triplet manifold [23,28]. According to the energy gap law [29] and considering a typical radiative lifetime on the order of 30 s [30,31], the phosphorescence quantum yield is expected to be approximately 10^{-4} . To enhance this yield, we employed perdeuterated perylene in place of the protonated analog, as deuteration is known to modestly reduce the internal conversion rate [32].

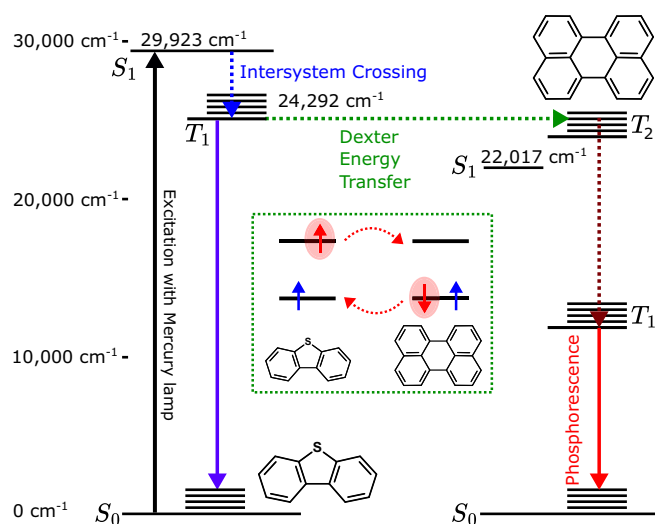


FIG. 3. Intermolecular enhancement scheme for perylene phosphorescence. This Jablonski diagram depicts the energy levels of dibenzothiophene on the left side and perylene on the right side. To increase the rate of phosphorescence for perylene, the host material is excited by UV light from a mercury lamp to S_1 . Through intersystem crossing, dibenzothiophene can then end up in the triplet state T_1 . These nonbound triplets, i.e., excitons, diffuse by Dexter energy transfer until they are trapped in a lower energy state (X-trap), which can be, for instance, a perylene molecule. The Dexter energy transfer between dibenzothiophene and perylene is here shown by the hypothetical route via T_2 of perylene. In addition, T_1 can still be involved in the transfer process.

Nonetheless, not all excitation photons are absorbed, and only a minute fraction of the resulting phosphorescence photons are detected in our setup. Accounting for all contributing factors, we estimate an upper limit for the detection probability of phosphorescence photons per singlet excitation event to be on the order of a staggeringly low 10^{-13} . Increasing the excitation power is not a viable solution, as higher intensities promote reverse intersystem crossing, leading to an increased nonradiative decay from the triplet states in this host-guest system [23].

To overcome these limitations and increase triplet generation efficiency without compromising the phosphorescence signal from perylene, we explored whether the dibenzothiophene host could be exploited to produce triplet excitons capable of migrating to perylene molecules. This concept is illustrated in the Jablonski diagram of Fig. 3. Literature reports place the singlet and triplet states of dibenzothiophene at $29\,923\text{ cm}^{-1}$ (334.3 nm) and $24\,292\text{ cm}^{-1}$ (411.8 nm), respectively [33], both lying energetically above the singlet state of perylene ($22\,017\text{ cm}^{-1}$; 454.0 nm) and thereby avoiding intermolecular intersystem crossing. The intersystem crossing rate of dibenzothiophene was found to be enhanced, possibly by a heavy-atom effect associated with its central sulfur atom [34], and as a result, dibenzothiophene exhibits relatively strong phosphorescence even at room temperature [35].

To populate triplet states in perylene impurities, energy transfer from the triplet state of dibenzothiophene can proceed via Dexter-type transfer [36], which relies on wavefunction overlap between donor and acceptor. However, this

mechanism is typically efficient only when the energy gap between donor and acceptor triplet states is small [37]. Previous studies demonstrated that a large gap reduces the probability of transfer, though increasing the concentration of trap molecules can partially compensate for this limitation [38]. Interestingly, quantum-chemical calculations suggest that perylene possesses a higher triplet state, T_2 , located only $\sim 0.2\text{ eV}$ ($\sim 1600\text{ cm}^{-1}$) above its singlet state in vacuum [39]. If this small energy gap is preserved upon incorporation into a dibenzothiophene matrix, the T_2 state could lie below the triplet state of dibenzothiophene and thus facilitate efficient Dexter transfer.

When applying the excitation scheme of Fig. 3 at low temperatures ($< 4\text{ K}$), we observe an intense and long-lived phosphorescence from dibenzothiophene in the delayed emission signal. The recorded spectrum [Fig. 4(a)] reveals narrow emission lines arising from isolated defect sites within the dibenzothiophene crystal lattice, commonly referred to as X-traps [34]. The vibrational structure of this spectrum closely matches previously reported data [33], although the observed linewidths ($\sim 8 \pm 2\text{ cm}^{-1}$) are somewhat broader than those reported for high-quality crystals ($\sim 1.5\text{ cm}^{-1}$) [34], likely due to reduced crystal quality resulting from rapid quenching in liquid nitrogen.

Phosphorescence decay kinetics [Fig. 4(b)], measured with a single-photon counter after mechanically blocking the excitation light, were fitted to a triple-exponential function, yielding time constants of 0.24 ± 0.03 , 0.68 ± 0.01 , and $4.7 \pm 0.3\text{ s}$. These values are consistent with literature reports [34]. Notably, as the temperature increases above 4 K, the dibenzothiophene phosphorescence signal diminishes rapidly. This behavior contrasts with undoped dibenzothiophene, where phosphorescence persists up to 77 K [34], and is likely due to transfer of the triplets to impurities.

Surprisingly, the delayed emission spectra vary significantly between samples, depending on the section of the zone-refining tube from which the dibenzothiophene was sourced. This variation is likely due to presence of concentration gradients of impurities introduced during zone refining. Among the impurities, we identified fluorene by its zero-phonon line at 424 nm and associated vibrational fingerprint (Fig. S3 in the Supplemental Material [24]), along with two unidentified impurities producing redshifted emission at 476 and 672 nm (Fig. S4 in the Supplemental Material [24]). Notably, the latter result demonstrates that it is possible to observe emission from impurities bridging a substantial energy gap between the host's triplet and impurities' triplet states.

Only material collected from the most purified section of the zone-refining tube yielded a phosphorescence spectrum consistent with that of perylene. This phosphorescence spectrum, integrated over 45 min [Fig. 4(d)], exhibits a clear zero-phonon line and a vibronic progression involving the 346 cm^{-1} long-axis stretching mode of perylene, also observed in the fluorescence spectrum [Fig. 4(c)]. The main zero-phonon line, corresponding to the $T_1 \rightarrow S_0$ transition, is located at $12\,756\text{ cm}^{-1}$ (784.2 nm), calibrated against krypton lamp emission lines. Several sidebands shifted by approximately 69 cm^{-1} , namely, 345 and 414, 1376, and 1455 cm^{-1} are observed. Notably, some of these sidebands, absent in the fluorescence spectrum, likely originate from different

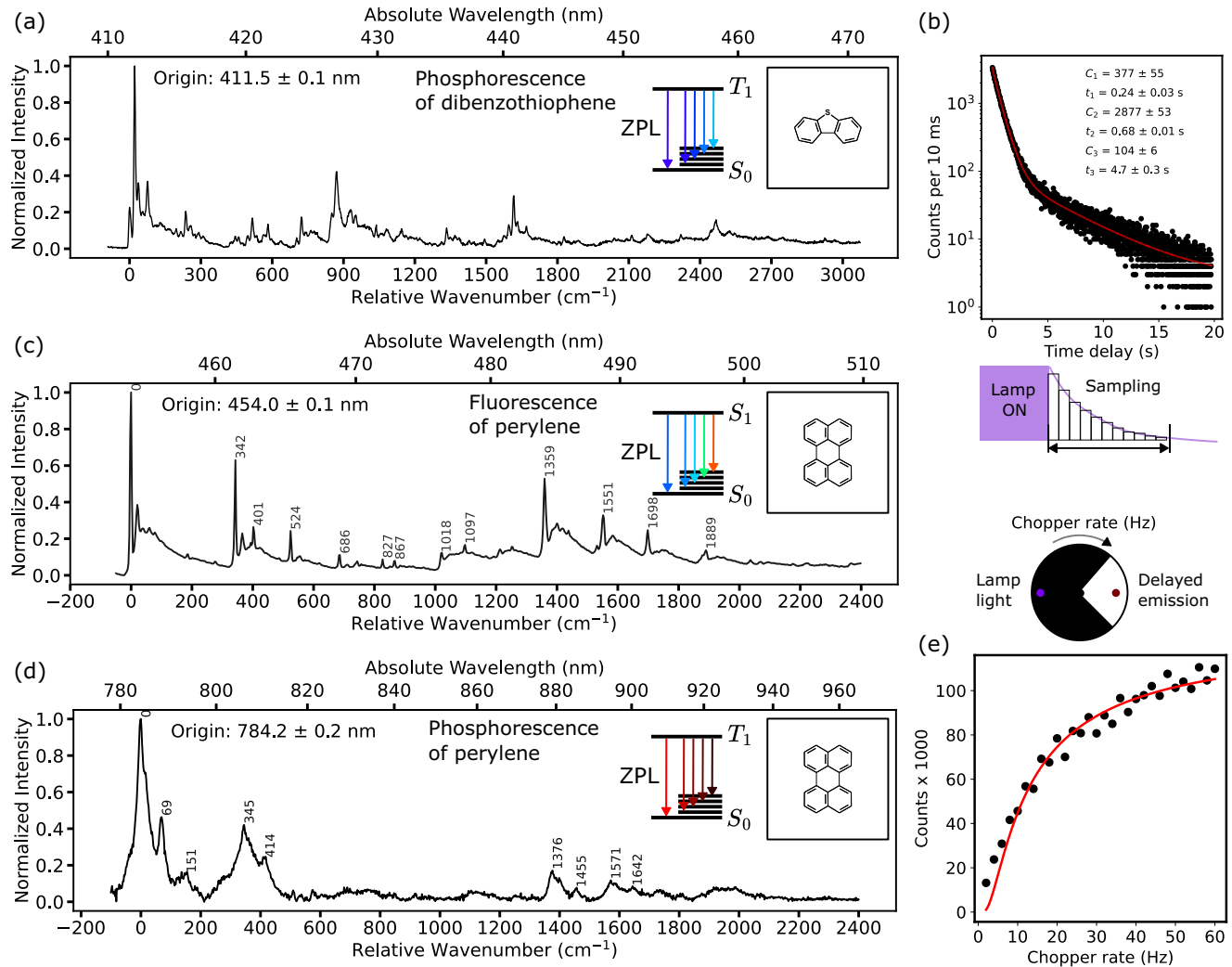


FIG. 4. Spectroscopic properties of ensembles of perylene and dibenzothiophene molecules. The phosphorescence spectrum of dibenzothiophene is shown in panel (a). The spectrum's origin corresponds to the main zero-phonon line. Panel (b) shows that the intensity of the phosphorescence of dibenzothiophene decreases multiexponentially over time, as indicated by the number of photons counted at time intervals of 10 ms after blocking the excitation light from the mercury lamp with a mechanical shutter. This measurement was repeated ten times and then averaged to yield the depicted decay curve. The fit parameters of the triexponential decay are displayed in the figure. Panels (c) and (d) compare the fluorescence and phosphorescence spectra of perylene. The fluorescence was measured with excitation at 447 nm, the phosphorescence with the mercury lamp and chopper rotating at 18 Hz. Panel (e) shows that the phosphorescence decay of perylene is measured differently than in panel (b) and makes use of the chopper. As perylene's phosphorescence is mixed up with other long-lived signals (see for reference Fig. S5 in the Supplemental Material [24]), the phosphorescence decay is measured indirectly by varying the optical chopper rate and recording a spectrum. The intensity curve is then fitted with Eq. (3) in the Supplemental Material [24]. The vertical axis denotes the number of counts measured in the spectrum over the course of 1 min.

spectroscopic sites identified in Fig. 2. For instance, the fluorescence site at 454.1 nm (Site 2) may correspond to phosphorescence at 788.4 nm, while the weak feature at 793.2 nm could relate to the redshifted site at 455.5 nm (Site 3). We note that the linewidths of spectral features in the phosphorescence spectrum (~ 30 cm⁻¹) are considerably larger than those for the fluorescence spectrum (~ 10 cm⁻¹). This could be the result of multiple factors: namely, the high concentration of perylene used for the phosphorescence experiment, a narrow-band excitation source was used to obtain the fluorescence spectrum, and the phosphorescence emission was collected from a much larger area. All of them can explain the inho-

mogeneity observed in the phosphorescence spectrum. Most importantly, inhomogeneities are filtered out in the fluorescence spectrum by the narrowband excitation, whereas the energy transfer to perylene molecules likely occurs over a broad range of energies, covering all sites.

By varying the chopper wheel frequency, we controlled the delay between the excitation pulse and detection window, set at one-quarter of the chopper cycle. The phosphorescence decay was analyzed by integrating the signal over different sections of the decay curve as a function of the chopper rate. The resulting data were fitted to a model described in Eq. (3) in the Supplemental Material [24]. The single exponential fit

results in a triplet lifetime of 36 ± 2 ms, and is longer than the shortest of the two lifetimes that were previously observed in single-molecule experiments (8.5 ± 0.4 and 64 ± 12 ms) [23]. The presence of only a single lifetime may indicate dominance of the T_z state in the phosphorescence, which due to its longer lifetime is expected to have a higher quantum yield of phosphorescence. A single phosphorescence lifetime was also found by Walla *et al.* [26].

Finally, we establish an upper bound for the triplet energy transfer efficiency from dibenzothiophene to perylene. Under identical spectrometer settings and a setup corrected for chromatic aberration, dibenzothiophene phosphorescence at low temperature yielded approximately 7.7 million counts/s, compared to only 1000 counts/s for perylene. Accounting for differences in phosphorescence quantum yields—estimated from triplet lifetimes and a radiative lifetime of 30 s to be 0.8%–1.6% for the T_x and T_y states and 16% for the T_z state of dibenzothiophene, consistent with room-temperature values of 2%–3% [40]—we estimate the phosphorescence quantum yield of perylene to be 0.03% for the T_x and T_y states and 0.2% for the T_z state. Assuming comparable detection efficiencies for blue and near-infrared emission, we derive an upper limit of approximately 1% for the triplet energy transfer efficiency. In practice, this value may be somewhat lower due to the higher detection efficiency for near-infrared photons. Nevertheless, considering the substantial energy gap between the triplet states of dibenzothiophene and perylene, this relatively high efficiency suggests the possible involvement of an intermediate triplet state, such as T_2 , in the energy transfer dynamics.

We note that the significant energy gap between T_2 and T_1 could promote triplet-triplet fluorescence over nonradiative decay. To exclude that the observed emission at 784.2 nm is a signature of delayed triplet fluorescence, we argue that the total energy of the exciton of dibenzothiophene is $24\,292\text{ cm}^{-1}$ and minus the observed zero-phonon line at $12\,756\text{ cm}^{-1}$ this leaves an energy of $11\,536\text{ cm}^{-1}$, equal to 867 nm or higher if part of the energy is transformed into heat. This wavelength is far off from the expected wavelength for the $S_0 - T_1$ energy gap. Moreover, as we detect a millisecond-range phosphorescence decay, recorded at delays of several milliseconds, we would effectively filter out the likely short-lived $T_2 - T_1$ fluorescence. If the long-lived triplet of dibenzothiophene would supply excitons during its entire lifetime—on the order of seconds—the delayed luminescence would have a decay of longer than milliseconds. This argument also agrees with our assumption that the transfer of triplet excitons happens instantaneously compared to the triplet lifetime of perylene [used to obtain Eq. (8) in the Supplemental Material [24]].

With the triplet's identified wavelength of 784.2 nm, an inhomogeneous broadening of 30 cm^{-1} , and precision of about 3 cm^{-1} , we have substantially narrowed the spectral region for locating a dark resonance to the triplet state. Further improvements in spectral precision may be achieved by enhancing crystal quality through sublimation growth, which could reduce the inhomogeneous broadening of spectroscopic sites below 1 cm^{-1} [41]. As a logical next step, we propose a targeted experiment to directly identify the dark resonance of a single molecule by monitoring its fluorescence intensity while scanning a near-infrared laser across the refined wavelength region.

IV. CONCLUSION

In this work, we have demonstrated that the detection bottleneck for the ultraweak phosphorescence of guest molecules can be solved by using the host material as a source for triplet excitons. Moreover, we found that the efficiency of triplet energy transfer strongly depends on crystal purity, in order to make the intentional impurities, i.e., guest molecules, the dominant acceptor for triplet excitons. Our used method holds promise for application in other host-guest systems, in particular for hosts that can strongly phosphoresce themselves. A likely candidate is terrylene in [1]Benzothieno[3,2-b][1]benzothiophene (BTBT) [42], having a similar structure to dibenzothiophene and displaying phosphorescence by UV excitation [43]. With our experiment, we have laid a basis for future experiments that continue with the perylene in dibenzothiophene system for finding the weak resonance to the triplet manifold, to aid all-optical spin manipulation in single molecules.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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