



Pentacene in 1,3,5-Tri(1-naphthyl)benzene: A Novel Standard for Transient EPR Spectroscopy at Room Temperature

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Received: 31 May 2021 / Revised: 15 August 2021 / Accepted: 16 August 2021 /
Published online: 7 September 2021
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Abstract

Testing and calibrating an experimental setup with standard samples is an essential aspect of scientific research. Single crystals of pentacene in *p*-terphenyl are widely used for this purpose in transient electron paramagnetic resonance (EPR) spectroscopy. However, this sample is not without downsides: the crystals need to be grown and the EPR transitions only appear at particular orientations of the crystal with respect to the external magnetic field. An alternative host for pentacene is the glass-forming 1,3,5-tri(1-naphthyl)benzene (TNB). Due to the high glass transition point of TNB, an amorphous glass containing randomly oriented pentacene molecules is obtained at room temperature. Here we demonstrate that pentacene dissolved in TNB gives a typical “powder-like” transient EPR spectrum of the triplet state following pulsed laser excitation. From the two-dimensional data set, it is straightforward to obtain the zero-field splitting parameters and relative populations by spectral simulation as well as the B_1 field in the microwave resonator. Due to the simplicity of preparation, handling and stability, this system is ideal for adjusting the laser beam with respect to the microwave resonator and for introducing students to transient EPR spectroscopy.

Prof. Dr. Christopher W. M. Kay would like to thank Prof. Dr. Klaus Möbius for giving him the chance to work at the Institut für Experimentalphysik at the Freie Universität Berlin from 1993 to 2005.

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1 Introduction

The combination of laser excitation and electron paramagnetic resonance (EPR) spectroscopy is a powerful approach for the detection of paramagnetic intermediates. Transient or time-resolved EPR (TREPR) [4, 14, 41] is, therefore, regularly employed in a growing number of laboratories to detect short-lived states including triplets, quintets [35] and radical-pairs [6] in, for example, proteins [43], materials for organic electronics [5, 42] or quantum information science [27]. In the field of dipolar spectroscopy and double electron–electron resonance (DEER) photoexcited triplet states offer the possibility of measuring distances in proteins rather than using conventional nitroxide spin-labels (e.g., (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl, TEMPO) [2, 3]. From these techniques, further highly specific experimental methods can be derived. Magnetophotoselection [26, 33, 39], for example, allows the investigation of the supermolecular arrangement of molecules and hyperfine spectroscopy [38] can be used to investigate the supramolecular interactions within a molecule. The underlying triplet-state physics and an introduction into TREPR instrumentation and spectrum analysis is given in literature [41].

Subsequent to the initial demonstration of TREPR spectroscopy in crystals of fluorene doped with phenazine [17], the triplet state of pentacene diluted in single crystals of *p*-terphenyl (see Fig. 1 for molecular structures) was observed following pulsed laser excitation [18]. The kinetic traces derived from the TREPR experiments are often used to characterize the performance of the EPR spectrometer. For example, the conversion of incident microwave power, P_{MW} , to B_1 -field [19] in the microwave resonator may be determined by analyzing the Torrey oscillations [36, 40], which are also referred to as transient nutations [41]. Knowledge of B_1 is crucial for obtaining a quantitative comparison of samples, since it depends the resonator's bandwidth, $\Delta\nu$; and thus its Q value which in turn is affected by the dielectric properties of the sample in addition to P_{MW} . These parameters are connected *via* the conversion efficiency C' of a resonator according to Eq. 1 [13].

$$B_1 = \frac{C' \sqrt{P_{\text{MW}}}}{\sqrt{\Delta\nu}}. \quad (1)$$

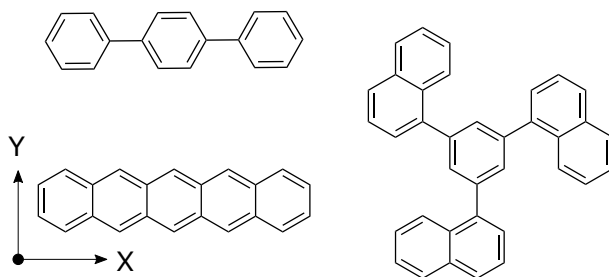


Fig. 1 Structures of pentacene with its main axes (left, bottom) and TNB (right) and *p*-terphenyl (left, top)

Alternatively, the conversion factor C directly converts the incident microwave power to B_1 field without reference to the bandwidth according to Eq. 2:

$$B_1 = C \cdot \sqrt{P_{\text{MW}}}. \quad (2)$$

Due to low solubility of pentacene in *p*-terphenyl, the maximum concentration is around 0.1%. Below this limit, pentacene molecules randomly replace *p*-terphenyl molecules with the long axis of the pentacene parallel to the long axis of the displaced host molecule [20, 21]. For crystal growth either co-sublimation [20, 23] or the Bridgman method is widely used [1, 12]. Both methods require specialist equipment which means that samples of *p*-terphenyl doped with pentacene cannot be prepared in many laboratories.

The resulting single crystal of *p*-terphenyl has three major orientations corresponding to the crystallographic axes, and as was shown by Kim and Weissman, their orientation relative to the external magnetic field, B_0 , is crucial for the signal intensity and the nutation pattern [18]. Thus the orientation of the crystal with respect to the external magnetic field must be carefully adjusted in the spectrometer by TREPR experiments. Indeed, misalignment of the crystal may decimate both the signal intensity and the amplitude of the Torrey oscillations.

From a more practical aspect, single crystals of pentacene in *p*-terphenyl are often employed to align the laser beam in order to optimize photoexcitation of the sample in the microwave resonator. However, this has the disadvantage that the laser beam is directed towards a point sample rather than the extended volume typically occupied by frozen solutions or thin film samples. To avoid this issue, a crushed crystal of pentacene in *p*-terphenyl is sometimes used for laser alignment. This provides a pseudo-powder sample—with essentially no preferred orientation—so that finding a signal is easier. The caveat is that the penetration of light into the crystalline powder is poor, and hence the TREPR signal is relatively weak [7]. By melting and resolidifying a mixture of *p*-terphenyl and pentacene directly within an EPR-tube, a polycrystalline sample is obtained that avoids most of the problems associated with doped single crystals but shows some orientation dependency in the magnetic field.

Here, we present 1,3,5-tri(1-naphthyl)benzene (TNB) as a host matrix for pentacene, see Fig. 1. TNB is a glass-forming compound, which melts around 459 K, and with a glass-transition point at 342 K [11, 24]. Not only does pentacene dissolve easily in liquid TNB, but in the absence of oxygen it is also stable at the melting point of TNB. Thus, sample preparation only requires that the two components are mixed together in the desired ratio, melted using a heat gun or oil bath under anaerobic conditions, and then cooled back down to room temperature. Because the short-range order of the liquid state is maintained in glassy samples, not only is the sample optically transparent but the solute molecules do not become aligned; as typically occurs in crystalline matrices [15, 16].

As we show below, not only does this system give rise to a well-resolved TREPR spectrum complete with Torrey oscillations, but more importantly it may be prepared in laboratories equipped with standard equipment [8, 28]. Together, these properties make pentacene dissolved in TNB a suitable test sample for TREPR measurements at room temperature. In addition, it may be used a standard sample

for calibrating or adjusting the TREPR spectrometer, as well an educational sample for students learning about TREPR spectroscopy.

2 Results and Discussion

It is often advantageous to excite chromophores near the maximum optical absorption. The UV–Vis spectrum of pentacene in TNB at room temperature is depicted in Fig. 2. The maximum is close to 590 nm. Nevertheless, there is still reasonable absorption at other widely available wavelengths, such as the second and third harmonics of a Nd:YAG laser, 532 nm and 355 nm (see Fig. 2 in SI).

Figure 3 depicts a representative two-dimensional data set of the photoexcited triplet state of pentacene in TNB at room temperature. The spectrum is powder-like and exhibits Torrey oscillations that are B_1 dependent. Time traces at the absorptive and emissive extrema (Fig. 3, right) are different in their oscillatory behaviour due to the magnetic field dependent dynamics of the system [36]. They follow a Bessel function of zeroth order and contain information about spin relaxation. Using a Fourier transform of the high-field transition starting at the first minimum, the nutation frequency ν_n was extracted to obtain the B_1 -field following the equation $\nu_n = \sqrt{2}\gamma_e B_1$, where the factor $\sqrt{2}$ arises due to the $S = 1$ nature of the spin system. By recording the kinetic traces as a function of P_{MW} , the frequency of the Torrey oscillations may be related to the square root of the microwave power (see Fig. 1 in SI) and thus the conversion factor, C , of the resonator may be determined. In this study, C was found to be $4.7 \text{ G}/\sqrt{W}$ which is comparable to the value of $4.2 \text{ G}/\sqrt{W}$ specified by Bruker.

A slice through the two-dimensional data set parallel to the magnetic field axis at the time of maximum signal intensity reveals the powder spectrum of the triplet state of pentacene. The zero-field splitting parameters may

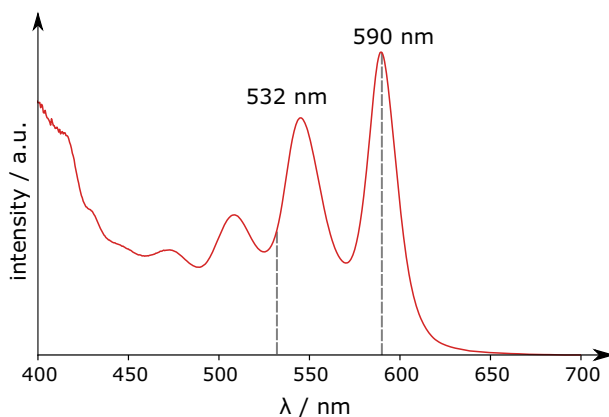


Fig. 2 UV–Vis spectrum of pentacene in TNB glass with indicated positions of the global maximum of the absorption (590 nm) and the second harmonic (532 nm) of a Nd:YAG-Laser

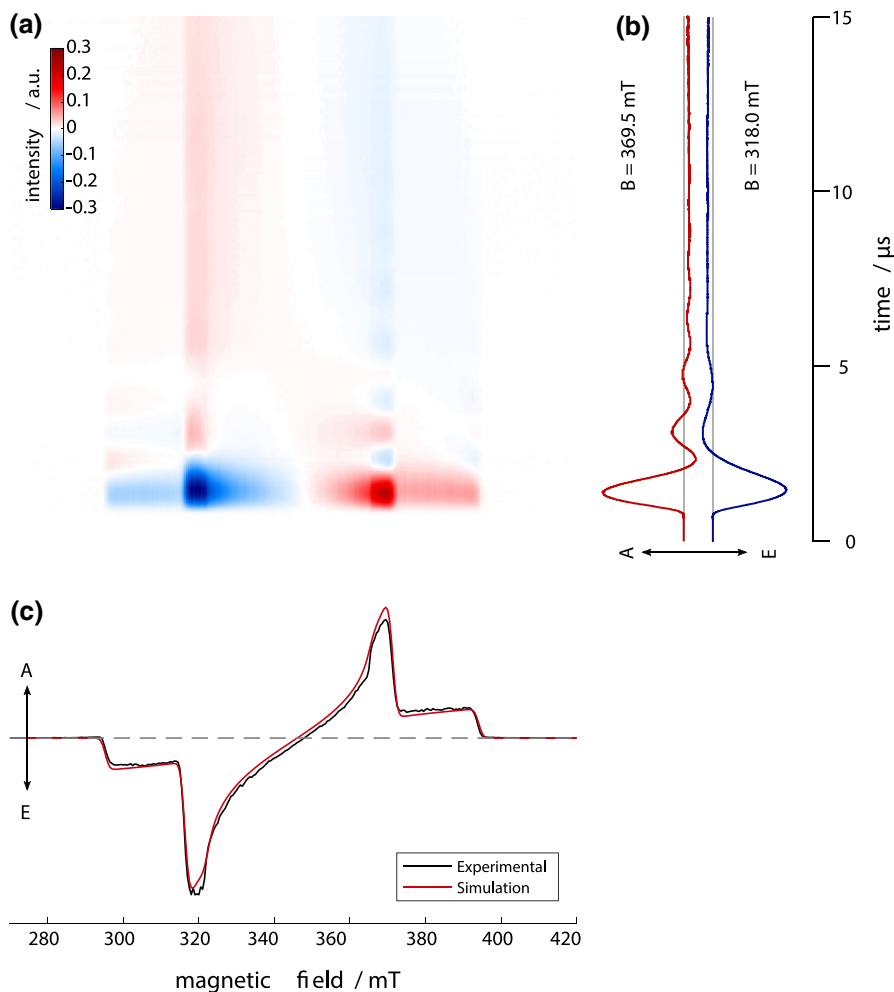


Fig. 3 2D TREPR spectrum of pentacene in TNB with the time traces through the respective extrema (right) and an average over 600 ns along the magnetic field axis (bottom) centered at 1.4 μs, excited at 600 nm together with a simulation

be extracted by simulation [25, 37]. The values of $|D| = (1385 \pm 4)$ MHz and $|E| = (50.6 \pm 1.3)$ MHz are similar to those found for pentacene in *p*-terphenyl crystals [22, 29, 44, 45] and thin films [23]. Surprisingly, the relative populations $p_1 : p_2 : p_3 = 0.19 : 0.35 : 0.46$ differ substantially from literature values of pentacene in *p*-terphenyl ($p_1 : p_2 : p_3 = 0.08 : 0.16 : 0.76$) [34, 44], indicating that the environment has a strong effect on the relative rates of intersystem crossing to the three triplet sub-levels.

In contrast to the spectra obtained in single crystals, where the peaks are narrow and depend strongly upon the crystal orientation with respect to the external magnetic field, the powder spectrum stretches over the full 2D range.

Consequently, there is no need to precisely hit a resonant magnetic field position when using the glassy sample to adjust the laser beam. Moreover, to obtain the essential triplet parameters of the molecule, only a single spectrum needs to be recorded rather than a complete rotation pattern with respect to the three canonical axes. These aspects are helpful not only for teaching TREPR, but also for introducing the concept of a powder pattern, which is generally the case for the TREPR spectra of randomly oriented triplet states in frozen solution.

The TREPR spectra presented here were recorded at room temperature. However, when the temperature is lowered the relaxation rates slow and hence the decay of the spin polarization also slows. We have tested the sample down to 80 K at which temperature it still gives an intense TREPR spectrum (data not shown).

3 Conclusion

We have shown that pentacene dissolved in glassy TNB is a useful TREPR standard. The broad powder-like spectrum and decent signal to noise ratio of the triplet state means that it is well suited for optimizing and characterizing the TREPR spectrometer, adjusting the laser system, and as a (nearly) fail-safe educational sample for beginners in the field.

Due to the ease of preparation and powder-like TREPR spectrum, pentacene in TNB is clearly superior to a single crystal of pentacene in *p*-terphenyl as a standard sample. Finally, because TNB is glass-forming and readily dissolves non-polar substances, it may turn out to be a convenient and useful alternative host matrix for TREPR spectroscopy of other aromatic molecules at room temperature, and find use in other applications, such as zero-field room-temperature masers [9, 10, 30, 32].

4 Experimental

4.1 Sample Preparation

A sample consisting of 0.01 wt% pentacene as prepared by literature methods [31] in 1,3,5-tri(1-naphthyl)benzene (TCI Germany) was prepared by mixing the two powders and grinding in a mortar. The sample was placed in a synthetic-quartz EPR-tube (3 mm inner diameter, QSIL Ilmasil), evacuated and flushed with argon several times. Subsequently, the mixture was heated to 195 °C under argon using an oil bath, at which temperature it forms a homogenous dark red liquid. The tube was removed from the oil bath and allowed to cool to ambient temperature, leading to the formation of a glass. The EPR-tube was evacuated at room temperature and flame sealed. Occasionally, the sample crystallizes, but the glass can easily be regenerated by melting the sample and subsequently cooling again.

4.2 UV-Vis Spectroscopy

A ground-up mixture of approximately 0.1 wt% pentacene and TNB was placed in a quartz cuvette with 1 mm path length and melted using an oil bath at 195 °C. After vitrification by allowing the sample to cool to ambient temperature, the glassy sample was measured on a Specord 210 Plus (Analytik Jena, Germany) in the range from 350 to 800 nm. A background correction was performed by subtracting the spectrum of the pure glassy matrix which was measured under the same conditions.

4.3 Time Resolved EPR Spectroscopy

TREPR spectra were recorded using a Bruker EMX spectrometer with a Bruker EMX premiumX microwave bridge and a dielectric-ring resonator (Bruker ER 4118X-MD5) which was placed in a closed-cycle cryostat (Cryogenic CF VTC) in a helium atmosphere. Time dependent signals were acquired using a digital oscilloscope (Teledyne LeCroy HDO9204) with a digitizing rate of 2 ns/8 bit.

Pulsed optical excitation was provided by an optical parametric oscillator (OPO) system (GWU primoScan/BB/120-INDI) pumped by a Nd:YAG laser (Spectra-Physics Quanta-Ray INDI PS 51/52) with a pulse width of approximately 6 ns, a pulse energy of 1.5 mJ and a shot repetition rate of 20 Hz. Each magnetic field point was recorded 100 times, wavelength dependent spectra were recorded with 1.0 mW microwave power and subsequently normalised to the same number of photons.

Processing and analysis of the time traces were performed with self-written MATLAB[®]-routines. Simulation of the spectrum averaged over the maximum signal was performed using the Tsim-programme [25] which is based on the EasySpin [37] package for MATLAB[®].

Supplementary Information The online version supplementary material available at <https://doi.org/10.1007/s00723-021-01420-4>.

Acknowledgements The authors thank Yan Fett and PD Dr. Till Biskup (Saarland University) for interfacing the Teledyne LeCroy Oscilloscope and the EMX Spectrometer and Saarland University for financial support.

Funding Open Access funding enabled and organized by Projekt DEAL.

Declaration

Conflict of interest The authors declare that they have no conflict of interest.

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