Supporting Information for

Unraveling the Room-Temperature Spin Dynamics of Photo-Excited Pentacene in its Lowest Triplet State at Zero Field

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ZF-trEPR Setup

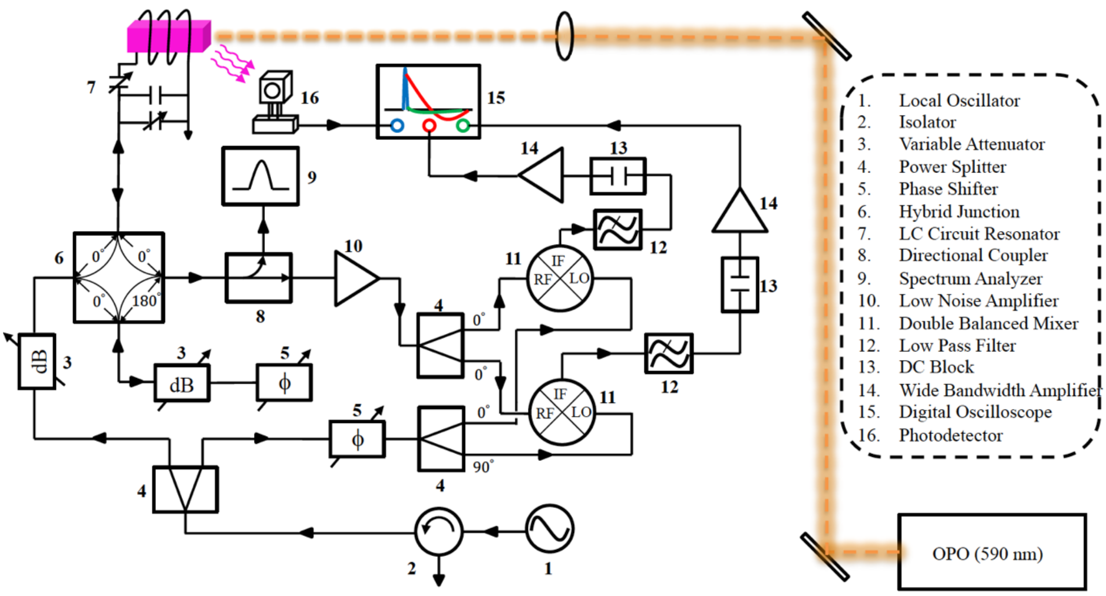

Figure S1. The block diagram of the home-built ZF-trEPR spectrometer.

Resonator

For ZF-trEPR measurements of the T_x-T_z, T_y-T_z and T_x-T_y transitions, the same pentacene doped *p*-terphenyl crystal was loaded within the coils (L) of two different LC resonators made of discrete components: (i) a tunable L-band resonator covering both 1.344 GHz (corresponding to T_y-T_z) and 1.450 GHz (T_x-T_z); (ii) a VHF resonator tunable (across a few MHz) over 106.5 MHz (T_x-T_y). The coils (solenoids) of both resonators were made of 1-mm copper wire, with an inner ("sample") diameter of 2 mm. Each coil was connected (soldered) in parallel to a bank (some tunable, some fixed) of low-loss capacitors (C) and critically coupled via a second adjustable capacitor to the end of a length of semi-rigid 50-ohm coaxially cable. The quality factor (Q) of each resonator (dominated by the ohmic surface losses of its copper coil) was around 30.

Microwave Drive

The microwave drive oscillator used in our ZF-trEPR spectrometer was a SynthNV DDS RF signal generator (WindFreak Technologies), tunable from 34 MHz to 4.4 GHz. Its output power was set at 13 dBm. Through several splitters and phase adjusters, this drove the reference arms of the I and Q mixers (each requiring 7 dBm) as well as driving the 4-port hybrid (= "magic tee") serving as an EPR bridge.

Signal Detection

Homodyne detection combined with I-Q demodulation were employed. A Keysight MSO-X 3104A oscilloscope (1 GHz bandwidth; 5 G samples s^{-1}) was triggered by stray light from the OPO's pulse measure by a DET 200 silicon photodetector (Thorlabs Inc.) terminated into 50 ohms at the oscilloscope's input. The signal from this detector was proportional to the OPO's instantaneous pump power, as applied to the maser crystal. At the same time, two of the oscilloscope's other input channels recorded the in-phase (I) and quadrature (Q) trEPR signals amplified by homebuilt broadband amplifiers (10 MHz bandwidth). The phase of the homodyne circuit's reference arm was adjusted to maximize the size of the I signal whilst minimizing that of the Q signal.

High-temperature Assumption for the Spin-Lattice Relaxation Rates

The upward and downward spin-lattice relaxation rates, w_{ij} and w_{ji} (i and j denote the sublevels of pentacene's lowest triplet state, T_1) obey the relationship ("detailed balance") [1]

$$\frac{w_{ij}}{w_{ji}} = e^{-\frac{|\Delta E|}{kT}},$$

where ΔE is the energy difference between the corresponding two sublevels, k is Boltzmann's constant and T is the absolute temperature. According to the known ZF splittings between the sublevels of T_1 at room temperature (298 K), the values of

w_{zx}/w_{xz}, w_{zy}/w_{yz} and w_{yx}/w_{xy} are 0.99977, 0.99978 and 0.99998, respectively. For the purposes of simulating the spin dynamics, the upward and downward spin-lattice relaxation rates across each transition within T_1 were therefore taken to be equal.

Fitting Procedures for the Spin Dynamics

For a given excitation power, the trEPR response as shown in Figure 3, was the average over 1024 consecutive trials (OPO shots) taking 102.4 seconds to complete (the averaging was done automatically by the digitizing oscilloscope). Each so-averaged trEPR response comprised a sequence of 2500 data points. To speed up the fitting analysis (which was performed using a *Mathematica* script), every 50 consecutive data points were then averaged down to a single data point, producing a sequence of just 50 points (at an approximant spacing of 4 μs). The trEPR signal represents the population difference between the measured transition's two sublevels; the signal $S_{ij}(t)$ can therefore be expressed as

$$S_{ij}(t)=N_i(t)-N_j(t)\ (i, j = x, y \text{ and } z)\#(S1)$$

Given that each excitation pulse from the OPO lasted just 5.5 ns, the populating process into the pentacene T_1 sublevels could be treated as instantaneous. The initial populations (at t = 0) of the three sublevels were set to

$$N_x(0):N_y(0):N_z(0)=P_x:P_y:P_z=0.76:0.16:0.08\#(S2)$$

Combining Eqs. S1-S2 with the master equation stated in the main text, the three trEPR signals were simultaneously fitted in *Mathematica*. The starting values of all six spin dynamics rates (k_i and w_{ij}) were chosen between 0 and 4.5×10^4 s^{-1} and only the fitted results with R-squared over 0.99 were used to calculate the stated estimates.

Reference

1. Matsuoka, H.; Retegan, M.; Schmitt, L.; Höger, S.; Neese, F.; Schiemann, O. Time-Resolved Electron Paramagnetic Resonance and Theoretical Investigations of Metal-Free Room-Temperature Triplet Emitters. *J. Am. Chem, Soc.* **2017**, *139*, 12968-12975.