Supporting Information

Perdeuterated Conjugated Polymers for Ultralow-Frequency Magnetic Resonance of OLEDs

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Supporting Information
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Experimental Procedures

S1 Fabrication of h-MEHPPV and d-MEHPPV OLEDs

The samples investigated in this study were produced as follows. From glass substrates covered with 100 nm of indium tin oxide, a stripe-shaped anode was defined by an etching procedure. A layer of poly(styrene-sulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) was spin-coated at a rotation speed of 2000 rpm resulting in a film thickness of 80 nm. A solution of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (h-MEHPPV) or of its perdeuterated analogue d-MEHPPV in toluene was prepared at a concentration of 6 mg/ml. The emissive layer was spin-coated at 2500 rpm from this solution to yield an approximately 70 nm thick polymer film. A 3 nm thick barium cathode covered by a 250 nm aluminum capping layer was deposited by thermal evaporation. To prevent the devices from oxidation they were encapsulated with two-component epoxy glue and a glass cover slip inside a nitrogen glovebox. OLEDs fabricated from h-MEHPPV or d-MEHPPV typically exhibit a turn-on voltage of approximately 3 V with the maximum intensity of electroluminescence at a wavelength of around 600 nm.

Results and Discussion

S2 Magnetoresistance response of h-MEHPPV and d-MEHPPV

The lifetime of the carrier pairs responsible for EDMR is finite. When the period of the RF radiation becomes longer than this lifetime, the RF radiation will act as a quasistatic contribution to the overall magnetic field, giving rise to magnetoresistance rather than magnetic resonance. To characterize the response of the two conjugated polymers investigated in this study to a static magnetic field \( B_0 \), magnetoresistance curves were recorded by sweeping \( B_0 \) from -1 to +1 mT. In Figure S1a, the resistance change \( \frac{\Delta R}{R} = \frac{R(B_0) - R(B_0 = 0)}{R(B_0 = 0)} \) is plotted against the static magnetic field \( B_0 \). Apart from the extensively studied decrease of resistance for increasing absolute values of the magnetic field, resulting from the suppression of hyperfine-induced mixing of singlet- and triplet-like spin pairs by the external field,[S1] an additional dip centered around \( B_0 = 0 \) mT is observed for both materials. This signature arises as a consequence of the so-called ultrasmall magnetic-field effect, where mixing between singlet and triplet states of charge-carrier pairs is increased due to crossings of hyperfine-split sublevels at low external magnetic fields.[S2] We find a much narrower response for d-MEHPPV in comparison to h-MEHPPV. As a consequence, a larger effect amplitude is observed for the given magnetic-field range for d-MEHPPV. The larger curvature of the magnetoresistance response of d-MEHPPV gives rise to a stronger effect of low-frequency quasistatic \( B_1 \) fields on the device resistance, as this additional field contribution can explore a larger part of the magnetoresistance curve. Since the value of the second derivative of the d-MEHPPV curve is greater than that of h-MEHPPV, so is the zero-field signal amplitude.

To illustrate the connection between the curvature of the magnetoresistance response and the EDMR spectra observed at low excitation frequencies, we differentiated the magnetoresistance curves for both materials numerically. The results, plotted in Figure S1b, show a pronounced peak centered around \( B_0 = 0 \) mT together with a region of negative curvature at finite \( B_0 \). As expected, an overall stronger effect is observed for d-MEHPPV. The EDMR signals at the lowest excitation frequencies (i.e., with the lowest influence of the Zeeman resonances) exhibit all of these properties. We are therefore confident that magnetic resonance experiments with driving-field periods longer than the effective lifetime of the charge-carrier pairs responsible for the spin-dependent recombination effects in part probe the curvature of the static magnetic-field response.
Figure S1. a) Magnetoresistance curves of h-MEHPPV (black line) and d-MEHPPV (red line) taken at a current density of 3.5 mA cm⁻². The deuterated compound shows a narrower and stronger response. The curvature (i.e., second derivative) of the magnetoresistance behavior (b) bears striking similarity to the low-frequency EDMR signals described in the main text, with a pronounced peak at zero field emerging, which is accompanied by an inversion of the signal at finite \( B_0 \).

S3 Assessment of hyperfine fields experienced by electron and hole spins

In organic semiconductor materials, the effective magnetic field at the site of a charge carrier is not exclusively determined by the externally applied magnetic field \( B_0 \), but is also influenced by the coupling of the charge-carrier spin to neighboring nuclei as described by the effective hyperfine field \( B_{hyp} \). The disorder distribution of these microscopic hyperfine fields for electron and hole spins, described by Gaussian functions, can be probed by magnetic resonance experiments: as the effective magnetic field is altered by the hyperfine interaction, so is the resonance field for each individual charge-carrier spin. Consequently, magnetic resonance spectra in OLEDs exhibit a line shape which is the superposition of two Gaussian functions, characterized by standard deviations \( \sigma_1 \) and \( \sigma_2 \), which can be taken as a measure of the hyperfine-field distribution experienced by electrons and holes and thus of the inhomogeneous broadening of the resonance.

We performed EDMR measurements at an excitation frequency of \( f = 280 \) MHz for h-MEHPPV and d-MEHPPV yielding spectra centered at \( B_0 = B_{EDMR} = \frac{\hbar f}{g \mu_B} = 10 \) mT as shown in Fig. S2. Here, \( \hbar \) is Planck’s constant, \( g = 2 \) is the \( g \)-factor of the charge-carrier spin and \( \mu_B \) is the Bohr magneton. The excitation power was kept low (63 mW for h-MEHPPV and 5 mW for d-MEHPPV) to avoid power broadening of the resonance lines. A clear separation of the resonance into two components, broad and narrow distributions, is apparent, especially for the protonated compound. Through the combination of high-field EDMR on h-MEHPPV and corresponding density functional calculations, the broader contribution could previously be assigned to electrons and the narrower one to holes.\[^{[S3]}\]

Here, by fitting the obtained resonance spectra with the superposition of two Gaussian functions, the hyperfine field distributions can be extracted for both materials. For h-MEHPPV, we find \( \sigma_1 = 0.862(42) \) mT and \( \sigma_2 = 0.186(11) \) mT, whereas the spectra are significantly narrower for d-MEHPPV with \( \sigma_1 = 0.288(10) \) mT and \( \sigma_2 = 0.091(11) \) mT. These values are in good agreement with the values previously reported for h-MEHPPV and d-MEHPPV.\[^{[S3, S4]}\] Remaining deviations can be attributed to inhomogeneities of the external magnetic field, residual power broadening (estimated to be < 15 \( \mu \)T for h-MEHPPV and < 5 \( \mu \)T for d-MEHPPV), and, to a minor extent, the onset of the \( \Delta g \)-effect in d-MEHPPV, leading to a slight frequency-dependent line broadening due to spin-orbit coupling.\[^{[S4]}\]
Figure S2. EDMR spectra of h-MEHPPV (a) and d-MEHPPV (b) recorded at $f = 280$ MHz and plotted against the difference of the external magnetic field $B_0$ and the resonance magnetic field $B_{\text{EDMR}} = 10$ mT. The spectra are well approximated by the sum of two Gaussians from which the width of the hyperfine-field distribution for the individual charge carriers – electrons and holes – can be extracted. To improve visibility, the number of points of the d-MEHPPV curve was reduced by a five-point binning.

S4 Determination of the offset of EDMR spectra arising from lock-in detection

The EDMR spectra shown in the main text are recorded with a lock-in amplifier. Because of inductive coupling of the RF excitation to the electrical circuit connecting the OLED to the power supply as well as carrier-pair transitions induced by the electric-field component of the RF radiation, a constant offset independent of magnetic field is superimposed on all recorded EDMR signals. This offset depends substantially on the RF power and the excitation frequency $f$, and to a very minor extent also on the angle between the static external magnetic field $B_0$ and the oscillating field $B_1$. For d-MEHPPV, the line shape of the Zeeman resonances is so narrow that the baseline of the EDMR signal can be identified with satisfactory accuracy within the sweep range of ±2 mT of the Helmholtz coils. This constant baseline is then simply subtracted from the measured data in Figure 1c, and in the right-hand panels of Figures 3 and 4 (note that Figure 2 shows unprocessed raw data for both materials).
For h-MEHPPV, the resonance peaks do not reach the level of the baseline at the extremal $B_0$ value of ±2 mT. To correct the recorded spectra of h-MEHPPV for the offset to allow for a dependable representation of the frequency- and power-dependent behavior of the Zeeman resonances and the zero-field peak, additional spectra were recorded for the excitation frequency and RF power values used in the main text. The measurement setup was modified so that it was possible to apply static magnetic fields of up to ±30 mT along the direction of $B_0 \perp B_1$, i.e., for $\alpha = 90^\circ$. For this magnetic-field strength, the baseline of the EDMR curve can be determined reliably. Figure S3 illustrates the procedure of the offset correction for the EDMR spectrum of h-MEHPPV displayed in Figure 1c of the main text. First, the baseline of the signal is determined to be $-10.1 \mu V$, as shown by the red dashed line in panel S3a. Together with a peak signal level of 19.35 $\mu V$ (green dashed line in panel S3b), this amounts to a total EDMR signal amplitude of 29.45 $\mu V$. As both the degree of inductive coupling and the signal amplitude vary between measurements at different points in time due to slight variations in the alignment of the setup and sample as well as sample degradation, it is necessary to determine the value of the EDMR signal at $B_0 = 2$ mT (orange crosses). With this information, it is possible to conclude which fraction of the signal amplitude is contained within the magnetic-field range of ±2 mT. This fraction amounts to 88% in the example presented. For the data displayed in Figures 1c and S3c, the measurement signal changes from $-1.02 \mu V$ at $B_0 = \pm 2$ mT to 40.02 $\mu V$ at $B_0 = 0$ mT within the available measurement range, leading to a full EDMR amplitude of 41.04 $\mu V/0.88 = 46.64 \mu V$. Accordingly, the offset was determined to be $-6.62 \mu V$. This value was then subtracted from the data to yield the spectrum shown in Figure 1c of the main text. This procedure was repeated for each of the EDMR spectra shown in Figures 3 and 4 of the main text. As another representative example, the result of the offset correction for the power dependence of the EDMR spectra of h-MEHPPV is illustrated in Figures S3d,e.

To compare the line shape of the EDMR signal for different values of the excitation power, after correction for the lock-in offset (Figures S3d,e), the spectra displayed in Figure 4 of the main text were normalized to the signal level of the Zeeman resonance, where the Larmor frequency of the spin equals the RF excitation frequency. This procedure is shown in Figure S3f and allows us to assess the evolution of the zero-field peak with RF power in comparison with the Zeeman resonance as discussed in the main text.

Figure S3. Illustration of the offset-correction procedure for h-MEHPPV OLEDs. a) From a separate measurement over a magnetic-field range of 30 mT, the baseline (red dashed line) of the EDMR signal is determined. In panel b), the peak signal at the Zeeman resonances is marked by a green dashed line. The signal level at $B_0 = \pm 2$ mT is indicated by orange crosses. c) With this information, the raw data (grey) is corrected to yield the spectra shown in the main text. The spectra shown in panels a)-c) were recorded with an RF excitation frequency of 8 MHz and a power of 8 W. d)-f) Offset correction and normalization of the spectra shown in Figure 4. The raw data (d) is first corrected for the offset of the lock-in amplifier (e) with the procedure described above. The resulting spectra are then normalized to their signal level at the Zeeman peaks to enable a meaningful comparison (f).
S5 Detection of Zeeman resonances at $f = 3.2$ MHz

As shown in Fig. 3 of the main text, two distinct regimes can be identified in the frequency-dependent behavior of the EDMR spectra: one where the Zeeman resonance at $|B_0| = \frac{\hbar}{g\mu_B}$ dominates the spectrum and a second one where only the zero-field peak is discernible. To detect the Zeeman resonance at as low a frequency as possible, the parameters of the measurement – integration time, device current and RF power – must be optimized such that the zero-field peak due to the quasistatic RF field contributions remains acceptably small. Fig. 4 of the main text shows that the zero-field peak grows rapidly with increasing RF power for d-MEHPPV. Therefore, a trade-off between signal quality (determined by device current and RF power) and zero-field peak amplitude must be identified. We found that at a power level of 0.2 W and a device current density of 1.75 mA cm$^{-2}$ it was possible to discern Zeeman resonances as distinct peaks at frequencies as low as 3.2 MHz. To do this, we averaged over sweeps of $B_0$ from $-2$ mT to $+2$ mT and back to $-2$ mT again, each measurement taking a total of 14 minutes. Figure S4 illustrates the gradual transition from well-resolved Zeeman peaks at 3.6 MHz to a dominance of the zero-field peak at 3.0 MHz. To increase peak visibility, each dataset was smoothed by a three-point moving-average filter. Note that the minimum frequency of 3.2 MHz at which a Zeeman resonance is resolved is only about twice as large as the Larmor frequency of an electron spin in Earth’s magnetic field.
SUPPORTING INFORMATION

Figure S4. EDMR spectra of d-MEHPPV at frequencies between 3.6 MHz and 3 MHz at a device current density of 1.75 mAcm⁻² and an RF power of 0.2 W. While for 3.6 MHz the Zeeman resonances are clearly resolved, the spectrum is dominated by the zero-field peak at 3.0 MHz.

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