S1. W-band CW-EPR spectra of light-induced polarons in polymer/blend drop-cast films

Figure S1: W-band CW-EPR spectra of a) P3HT/PCBM (1:2) and b) MDMO-PPV/PCBM (1:2) blends at $T=100K$ in the dark and with the light on. The * indicate the Mn(II) cavity background signal. The experiments are performed with a microwave power of 70 $\mu$W (P3HT) and 0.07 $\mu$W (MDMO-PPV). Modulation frequency: 100 kHz, Modulation Amplitude: 0.3 mT. The samples were illuminated with light with a wavelength of 488nm using a Ar$^+$ laser. Besides the polaron, a clear signal of the PCBM$^-$ radical is observed as reported earlier by J. De Ceuster et al., Phys. Rev. B, 64, 195206 (2001).
S2. Influence of deviation of the polymer chain direction from substrate plane

In order to determine whether the polymer chain direction can have a certain deviation angle from the substrate plane, while it still adopts all orientations within the substrate plane, the following approach was tested. Each orientation was given a probability determined by an orientational distribution function (ODF) that was in this case an oblate spheroid. In spherical coordinates, the ODF is given by:

\[
F(\alpha) = \frac{ab}{a^2 \cos^2(\alpha) + b^2 \sin^2(\alpha)}
\]

In which the angle \(\alpha (0\leq\alpha\leq\pi)\) is the azimuth of the polymer chain direction.

Each computed EPR spectrum takes into account all possible orientations (Euler angles calculated on spherical grid) of the molecular frame with respect to the magnetic field, weighted by the ODF. It is also possible to rotate the ODF over an angle \(\theta (0\leq\theta\leq\pi/2)\). The two extreme orientations are: film parallel to the magnetic field \((\theta=0^\circ)\) and perpendicular to the magnetic field \((\theta=90^\circ)\) (see Figure 3, main text).

The shape of the spheroid, i.e. the relative weights of different orientations, and hence the EPR spectral shape, is determined by the ratio \(b/a\). Taking \(a=1\), the flatness of the distribution is varied from \(b=0\), corresponding to the planar distribution, PD, discussed in the main text (as in Figure 3 of main text), to \(b=1\), or random distribution as in the simulations for the drop-cast material (Figure 2, main text). In Figure S2, simulations of CW-EPR spectra of P3HT and MDMOPPV assuming ODFs with varying flatness are compared to those for the planar distribution (PD). As expected, when \(b=1\), that is when the ODF is a sphere, the same simulation is found for both film orientations. Decreasing the flatness \(b\) leads to increasing difference between the two film orientations. Finally, for \(b=0.01\) in the case of P3HT and for \(b=0.001\) for MDMO-PPV, ODF and PD are equivalent. This convergence is slower for the parallel than for the perpendicular case for P3HT and faster for MDMO-PPV.

Comparison of Figure S2 with the experimental data allows determining an upper limit for \(b\):

\(b_{\text{max}} = 0.3\) (P3HT) and \(b_{\text{max}} = 0.1\) (MDMO-PPV). Although the use of an ODF improved somewhat the agreement with the experiment, a PD was used for the simulations of the angular variation of the spectra in Figure 3, because this reduces the calculation times considerably and reproduced the general features of the spectra in a satisfactory way.
Figure S2 Simulation of CW-EPR polaron signals of a) P3HT and b) MDMO-PPV for two directions of the spin-coated film. A comparison of the orientation distribution function for four values of the flatness parameter $b$ and for the plane distribution function (PD) (solid line) is shown. The corresponding g-values taken for the simulations are specified in the Table 1 (main text).
S3. Spin-density distributions from theoretical studies used for computation of the expected proton couplings in Table 2 and 3.

*Figure S3a:* Spin density distribution for a polaron in a thiophene oligomer extended over 13 rings (adopted from ref. [36]). In order to obtain the values listed in Table 2 (main text), this distribution has to be scaled with $\rho_C(0)/\rho_{\text{ring}}(0)$, whereby $\rho_{\text{ring}}(0)$ is the spin-density on the central ring as computed by DFT and $\rho_C(0)=0.042$ as determined from the maximal observed proton coupling.

*Figure S3b:* Maximum spin density per site (phenylene or vinylene) on single carbons obtained from a PPV model in reference [17], selecting only the H-bound carbons of the MDMO-PPV case. The carbon spin-densities not mentioned in this figure are negligible for the computation of the proton hyperfine parameters (contribute only to Larmor peak). Note that the polaron is centered on a vinylene site. **Note that the computed maximum value for the carbon spin density (~0.09) in PPV is very close to the experimental value of MDMO-PPV (0.074).**
S4. $^{13}$C X-band/Q-band HYSCORE and ENDOR analysis

**Figure S4**: Experimental Q- and X-band HYSCORE (blue) and Q-band ENDOR at T=20K on iodine-doped P3HT and MDMO-PPV drop-cast films. Overlaid to the HYSCORE spectra, a simulation (red) considering the hyperfine couplings indicated at the foot of each figure.
For the P3HT polaron, a hyperfine coupling to $^{13}$C was detected by X-band HYSCORE experiments on drop-cast samples (figure S4, left). Similarly, X band and Q-band HYSCORE spectra on drop-cast MDMO-PPV revealed $^{13}$C signals (figure S4, right). The HYSCORE ridges cross the diagonal at about 3.7 MHz ($^{13}$C Larmor frequency at X-band) and 12.7 MHz ($^{13}$C Larmor frequency at Q-band), respectively, indicating that the nuclei responsible for the interaction are indeed $^{13}$C. Furthermore, signals stemming from $^{13}$C interactions are detected in the Q-band Mims ENDOR spectra for both compounds (Figure S4, bottom).

$^{13}$C has a natural abundance of only 1.1 %. Therefore $^{13}$C interactions are hard to detect and usually $^{13}$C signals can only be observed when several magnetically nearly equivalent nuclei contribute.

This suggests that the observed $^{13}$C signals probably stem from the more abundant $^{13}$C nuclei with small hyperfine couplings and cannot be ascribed to the strongest $^{13}$C interactions. Indeed, if we try to interpret the observed signals in terms of one dominant interaction, we cannot reproduce any of the findings from the $^1$H ENDOR and HYSCORE data, as is shown below.

In the case the full $^{13}$C spectrum would be observed, the maximum derived carbon spin density should be at least as big as the one derived from the proton hyperfine data for the H-bound sp$^2$-hybridized carbons. As is shown in Figure S4, the observed spectra can in principle be simulated adequately in terms of a single axial hyperfine tensor. The isotropic part then stems from the s contribution to the spin density and the anisotropic part from the p contribution. In general, the anisotropic part can be separated into $p_s$, $p_y$ and $p_z$ contributions, but in this case, because of the $\pi$ bonds, we can neglect the $p_s$ and $p_y$ contributions. Comparing the experimental hyperfine values to the tabulated isotropic ($a_{iso} = 3110$ MHz) and anisotropic ($B = 90.80$ MHz) value for 100% spin density in the 2s or a 2p orbital of carbon, we can deduce the carbon spin density. Using the McConnell relation, an isotropic proton hyperfine interaction of the bound proton can be derived and compared to experimental proton hyperfine values.

### a) P3HT.

A good simulation of the $^{13}$C hyperfine coupling detected in the X-band and Q-band HYSCORE and ENDOR measurements can be achieved using a hyperfine tensor $A = [-0.4 -0.4 2] \pm 0.5$ MHz (Figure S4). If we consider that A has an isotropic and an anisotropic contribution, we have:

$$A = a_{iso} + A_{anisotropic} = a_{iso,2s} + A_{2p_z} = a_{iso} + \begin{pmatrix} -B \\ -B \\ 2B \end{pmatrix}$$

This leads to $a_{iso} = 0.4$ MHz and $B = 0.8$ MHz for the largest $^{13}$C interaction in the P3HT polaron. By comparing these values with the tabulated values we obtain $\rho_s = 1.3 \times 10^{-4}$ and $\rho_{pz} = 8.8 \times 10^{-3}$. The McConnell relation then allows for calculation of the isotropic proton hyperfine interaction: $a_H = Q \rho_C = -72 \times 8.9 \times 10^{-3} = -0.64$ MHz. This coupling lies in the order of the proton hyperfine couplings of the sites -4, 4, 4 (a$_{iso}$ = 0.65 MHz; $A = [-0.32 -0.97 -0.65]$ MHz) (Table 2, main text). Hence, the observed $^{13}$C signals do not stem from all carbons. It is expected from the low natural abundance of $^{13}$C and the larger anisotropy of the $^{13}$C hyperfine coupling that the strongest $^{13}$C couplings will lead to a very weak HYSCORE signal. In fact, detection of the contribution of a single $^{13}$C nucleus in natural abundance (1.1%) is not possible considering the noise level of the spectra. The observation of $^{13}$C HYSCORE and ENDOR signals in samples that were not $^{13}$C-enriched, like the molecules at hand, is entirely due to the fact that many $^{13}$C nuclei with approximately similar hyperfine interactions are contributing to the signal. We thus pick up only the signals of the many carbons that are far away from the polaron center (i.e. so-called remote
carbons, consisting of carbons from the polymer backbone (units -4,4 and further) and the polymer substituents). The weak contributions of the larger interactions are buried in the noise.

b) MDMO-PPV.

X-band $^{13}$C HYSCORE and Q-band $^{13}$C ENDOR measurements in randomly oriented samples also show hyperfine couplings of the same order as those for P3HT. The X-band $^{13}$C HYSCORE and Q-band ENDOR spectra could be simulated using $A=[-1.1 \ -1.1 \ 2] \pm 0.5$ MHz where a different hyperfine tensor seems to fit the Q-band HYSCORE patterns: $A=[0.5 \ 0.5 \ 4] \pm0.5$ MHz. This already indicates that we are not observing the full $^{13}$C pattern. Considering the largest hyperfine tensor $A=[0.5 \ 0.5 \ 4] \pm 0.5$ MHz, the corresponding $a_{iso}=1.7$ MHz and $B=1.17$ MHz. Comparison of these values with the ones tabulated yields $\rho_s=5.3 *10^{-4}$ and $\rho_{pz}=1.3 *10^{-2}$. The isotropic proton hyperfine interaction $a_H = Q \rho_C = -72 *1.3 *10^{-2} = -1.0$ MHz. For MDMO-PPV this coupling lies in the order of the hyperfine couplings of the phenylene protons at positions -5 and 5 and the vinylene protons at positions -6 and 6 ($a_{iso}=-0.59$ MHz; $A=[-0.30 \ -0.89 \ -0.59]$). Again, the observed $^{13}$C does not represent the full $^{13}$C interaction pattern, due to the low natural abundance of $^{13}$C and insufficient signal to-noise ratio to detect the carbon sites with a larger spin density. We again only pick up the signals of the many carbons that are further away from the polaron center (i.e. so-called remote carbons, consisting of carbons from the polymer backbone and the polymer substituents).