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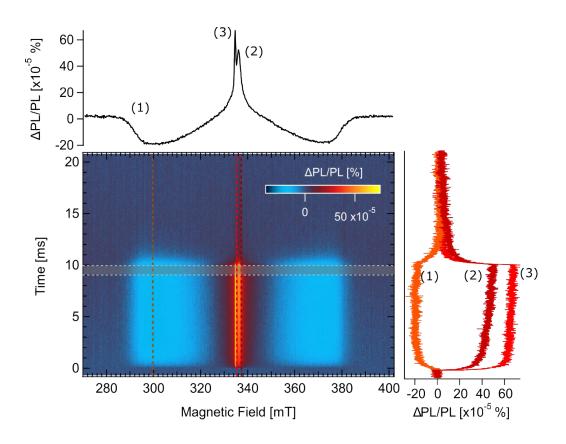
## SUPPORTING INFORMATION

for

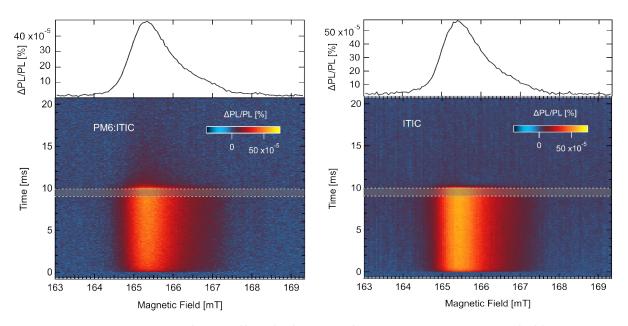
## Detecting triplet states in opto-electronic and photovoltaic materials and devices by transient optically detected magnetic resonance

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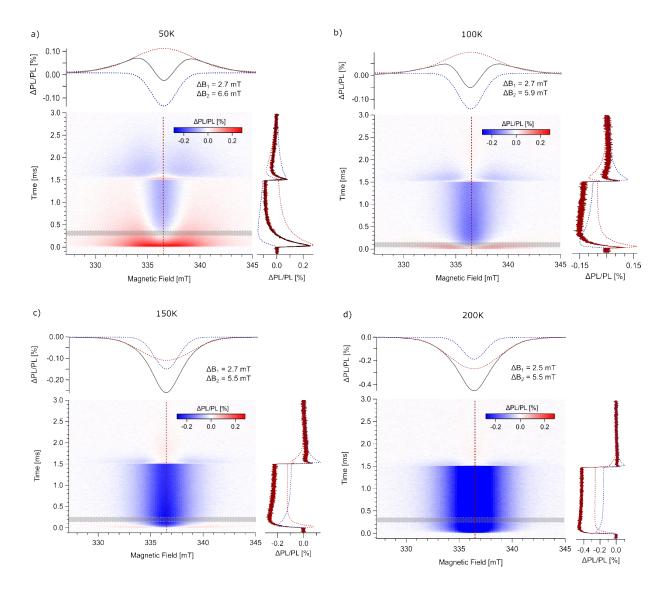
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**Figure S1.** Transient PLDMR of a pristine ITIC film with exemplary transients (right) and spectrum (top), averaged over 9-10 ms. There are three superimposed spectral contributions: (1) A wide "wing-like" pattern ( $^{\sim}100$  mT wide, D=1300 MHz) that can be assigned to molecular ITIC triplet excitons. (2) A central CT/PP peak at B=336.5 mT with (3) an additional narrow spike at 334.8 mT. Measured with 473 nm laser excitation at T=10 K and MW pulse length of 10 ms.



**Figure S2.** Transient PLDMR of the halffield (HF) signals of OPV blend PM6:ITIC blend (left) and pristine ITIC (right). Averaged spectra from 9 - 10 ms during microwave pulse are shown on top. Both signals have the same spectral position (g-factor), shape and comparable intensities. Measured with 473 nm laser excitation at T = 10 K and MW pulse length of 10 ms.



**Figure S3.** Transient PLDMR of OLED m-MTDATA:3TPYMB blend for 50 K, 100 K, 150 K and 200 K. During the 1.5 ms long microwave pulses, first, strong perturbations with changing signs are observed, before the intensities reach a new equilibrium under these conditions. Opposite trends are observed upon switching off the MW pulse. At all temperatures, signals of two triplet states and their time-dependent intensity traces can be extracted by a global fit with two Gaussian FWHM linewidths ( $\Delta B_1$ ,  $\Delta B_2$ ). The contribution of the narrower triplet signal  $\Delta B_1$  (blue) is always negative and switches sign afterwards. The contribution of the broader triplet signal  $\Delta B_2$  (red) is positive during the MW pulse at low temperatures and becomes more negative with increasing temperature or time. Measured with 365 nm LED excitation.