Supporting Information

Purely Organic Microparticles Showing Ultralong Room-Temperature Phosphorescence

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1. TCSPC

![TCSPC decays graph]

Figure S1: TCSPC decays of a PMMA:TCATPB thin film covered with Exceval, as well as P_{840} and P_{400} embedded in Exceval. IRF is the instrument response function.

2. XRD

XRD patterns were measured in ambient air by using a Bruker Advance D8 diffractometer equipped with a 1.6 kW Cu-Anode (\( \lambda = 1.54060 \ \text{Å} \)) and a LYNXEYE_XE_T 1D-Mode detector. The scans (2theta-Omega mode, \( 2\theta = 2°-60° \), step size 0.02°, 1 s/step) were measured in standard Bragg-Brentano geometry (goniometer radius 420 mm) and are background corrected.
3. Degradation

Degradation experiments were done using an Omnicure S2000 (Excelitas Technologies) equipped with 357 nm fluorescence bandpass filter (Edmund Optics) which yields an excitation intensity of 100 mW/cm$^2$. For comparison: The LED used for normal photoluminescence measurements has an irradiance of 2.6 mW/cm$^2$. For spectrum acquisition, a Thorlabs LED (M365LP1) with a 370 nm fluorescence bandpass filter (Edmund Optics) was used. For delayed spectra and decay curves, the standard setup (see experimental part) was used.

The degradation of the samples is quite fast at the beginning. After reaching a certain value, it is much slower. This is presumably due to remaining oxygen in the sample. If it is present, the sample degrades very fast. Once it is consumed it slows down. This is most probably the reason why the switching experiments (Figure 5) only show low degradation. Presumably, the samples are already degraded by illuminating with the laser. Interestingly, the phosphorescence lifetime strongly decreases over time. This is presumably due to a local heating of the sample and an increased permeability of the oxygen barrier. This would also explain why the phosphorescence decreases much faster than the fluorescence.

Figure S2: XRD pattern of quartz substrates covered with Exceval, P$_{840}$ in Exceval as well as P$_{400}$ in Exceval.
Figure S3: Lifetimes vs. cumulative dose (summed up optical energy reaching the sample) of P₈₄₀ and P₄₀₀ embedded in Exceval.

Figure S4: Intensity vs. cumulative dose (summed up optical energy reaching the sample) of P₈₄₀ and P₄₀₀ embedded in Exceval.

4. O₂ Sensitivity

Measurements have been performed with a self-built gas-mixing station. Mixing ratios were provided using mass-flow controllers (Bronkhorst, EL-FLOW select) and pure gases (Oxygen Linde O5, Nitrogen Linde N6). The resulted oxygen concentration was measured with an O₂-sensor (Pyroscience, FireSting O₂ equipped with trace flow-through cell). For
photoluminescence and delayed spectra as well as decay curves the standard setup (see experimental part) was used.

All spectra were acquired with a UV/VIS spectrometer (Cas 140CTS, Instrument Systems) utilizing sample's face emission. The transients were recorded with an amplified photodiode (PDA100A, Thorlabs) equipped with a longpass filter and read out by a multifunction lab instrument (STEMlab 125-14, Red Pitaya). The same instrument was used for triggering both the spectrometer and LED to obtain delayed spectra. All instruments were controlled with the use of SweepMe [1], a multi-tool measurement software.

[1] Fischer, A.; Kaschura, F. SweepMe!-A Multi-Tool Measurement Software (SweepMe.Net). 2016.

Figure S5: Emission spectra of P$_{840}$ in Exceval in dependence of the oxygen concentration.
5. Phosphorescent imaging of the particles

Figure S7: Schematic presentation of the data evaluation.
Figure S8: Raw data of one selected spot.

6. Activation of phosphorescence

Figure S9: Increase of phosphorescence and consecutive decrease of the fluorescence of P$_{840}$ embedded in Exceval by illumination with a 365 nm LED during a period of 5 minutes.
7. Determination of radiative and non-radiative rates

At a temperature of 77K, the nonradiative rates of the phosphorescence are 0. Therefore, the radiative rate can be calculated as

\[ k_r = \frac{1}{\tau_{77K}} \]  \hspace{1cm} (1)

At room temperature, the radiative rate has to be added:

\[ \frac{1}{\tau_{RT}} = k_r + k_{nr} \]  \hspace{1cm} (2)

The nonradiative rate can be calculated according to (1) and (2).