

Supporting Information

for

Dynamic Quenching of Triplet Excitons in Single Conjugated-Polymer Chains

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MATERIALS AND METHODS

Sample preparation and experimental setup:

Detailed information on the synthesis of the PhLPPP ladder polymer is reported elsewhere (for the chemical structure see Figure 2a of the main text with R₁: decyl, R₂: hexyl, M_w: 19600 g/mol, M_n: 14700 g/mol (Ref. [1]). BODIPY dyes were purchased from Sigma Aldrich (BODIPY493/503) and used without further purification. The molecules were dissolved in toluene solution, diluted to ~1 pM concentration and mixed with a 2 wt% PMMA/toluene solution. The analyte/PMMA mixture was spin coated (2min @2000rpm) onto cleaned borosilicate cover slips leading to well separated single molecules immobilized in a PMMA film of approximately 100 nm thickness. Prior to each measurement, blank PMMA samples were checked for fluorescent contaminations. Single molecule measurements were performed with a confocal microscope as described elsewhere (Ref. [2]). PhLPPP and BODIPY molecules were excited with fiber coupled diode lasers at 405 nm and 488 nm (Picoquant, LDH-Series- 405 and 488) with excitation power densities of 400 Wcm⁻² and 800 Wcm⁻², respectively. Photon antibunching measurements in Figure 2 were performed with a frequency doubled Ti:sapphire laser (Spectra-Physics, MaiTai-BB) to reduce the possibility for re-exciting the molecules within one laser pulse (Ref. [3]). PL traces of single PhLPPP(BODIPY) molecules were recorded over a fixed measurement time of 20 s (100 s) under exposure of the sample to dry nitrogen atmosphere to prevent triplet quenching by molecular oxygen. Reference measurements under air were taken to confirm the absence of the fluorescence blinking caused by STA (Ref. [4]).

Data analysis:

For PhLPPP and BODIPY, time windows of 100 ms and 500 ms were used to calculate photon correlation events up to a maximum correlation time $\Delta\tau_{max}$ of 1.2 ms and 2.5 ms, respectively. The longer integration time window for BODIPY dyes ensures that sufficient correlation events contribute to the histograms since the absorption cross section of the dye and therefore the strength of the PL signal is low compared to that of PhLPPP. An integration time of 500 ms is necessary to obtain a reasonable number of correlation events while maintaining a suitably small sampling rate in order to probe dynamics in the triplet-state population on the timescale of seconds. In addition, the average “off”-time, i.e. the triplet lifetime of the BODIPY dye (16 ms) (Ref. [2]), is also increased compared to PhLPPP, which demands a larger maximum correlation time $\Delta\tau_{max}$ to ensure that the decay of the correlation signal $C(\Delta\tau)$ with correlation time $\Delta\tau$ reaches saturation.

Each intensity time trace was binned in 1 ms intervals to extract the maximum count rate as indicated in Figure 2d to avoid averaging over multiple “off”-“on”-cycles of the fluorescence. Therefore, the maximum count rate of a single molecule is the same for regions (I) and (II).

For the estimation of triplet and polaron lifetimes, biexponential fits were applied to the full photon correlation curves as shown in Figure 5e to extract the photon bunching amplitudes due to the triplet and polaron dark states, B_T and B_P , as well as their decay times in the autocorrelation, $\tau_{ac,T}$ and $\tau_{ac,P}$. An upper limit of 2 s was estimated for the longest polaron lifetime that can be extracted with confidence from the dataset, because the correlation curves sample only a finite number of “on”-“off”-cycles on a timescale of seconds and the overall photostability of single PhLPPP molecules limits the number of blinking events due to polaron formation that can be recorded within one single-molecule PL intensity trace.

References

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