Experimental details

Samples were prepared by spin-coating solutions of 1 (10^{-10} M) and Zeonex (5 mg/mL) in chloroform (Aldrich, spectrophotometric grade) on a cover glass at 3000 rpm. This yields > 50 nm thick polymer films. Cover glasses were carefully cleaned before spin-coating by sonication in acetone, sodium hydroxide (10 %), and MilliQ water and by irradiation with UV light.

The set-up for the single-molecule experiments has been previously described.\textsuperscript{3} For 514/633 nm a dual band dichroic mirror was used (Chroma, model 51017). Excitation sources were an argon-ion laser (Spectra Physics Stabilite 2017) for \( \lambda_{\text{exc}} = 488 \) and 514 nm and a helium-neon laser (Spectra Physics Model 117A) for \( \lambda_{\text{exc}} = 633 \) nm. For all fluorescence traces a bin time of 5 ms has been employed. Single-molecule spectra were recorded on a liquid nitrogen cooled CCD-camera (Princeton Instruments) with a 5 s bin.

The polarization \( P \) was calculated using Equation 1 from \( I_\parallel \) (the intensity of the fluorescence with the polarization parallel to the excitation light), \( I_\perp \) (perpendicular polarization), and \( g \) (a correction factor that accounts for the difference in sensitivity for the detection of emission in the perpendicular and parallel channels).

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P = \frac{I_\parallel - gI_\perp}{I_\parallel + gI_\perp} \quad (1)
\]
Figure S1. Absorption (solid line) and TDI emission spectra (dashed line) of compound 1 in toluene. A PI emission spectrum (dotted line) is also shown, exhibiting good overlap with the TDI absorption bands.
Figure S2. Spectral evolution of the emission of a single molecule of 1 upon 488 nm excitation. After four spectra (20 s) a bleaching step occurs, neither changing the position of the emission maxima nor the shape of the spectrum. This is caused by bleaching of a PI chromophore (see text). Four spectra later the TDI chromophore bleaches and PI emission appears, which also bleaches after four additional spectra.
Figure S3. Parallel (black) and perpendicular (grey) channels of a fluorescence trace (bottom) of a single molecule of 1 ($\lambda_{exc} = 488$ nm) displaying step-wise bleaching. The mean value of the P-trace (top) does not change after a step has occurred. The noise on the P-trace is however higher for the lower levels. During the off-times (at 122 and 159 sec) P is not defined and varies wildly.