Supplementary Information

We investigated fluorescence spectra of single o-PDI and single no-PDI dyes in 8CB films deposited onto a SiO_2 substrate with a confocal microscope at 488 nm excitation. In comparison to ensemble experiments of the respective dye molecules in toluene, single molecule spectra in 8CB are shifted by about 10 nm to the red, which we attribute to a solvent shift caused by the electric dipole moments of 8CB molecules. The spectra in 8CB show typical single molecule features such as blinking and spectral diffusion (in case of no-PDI). The spectra of o-PDI in 8CB are somewhat narrower than those in toluene. Therefore we exclude a noticeable formation of aggregates, which would show spectral shifts and splittings. Aggregate formation, however, has been recently observed for o-PDI type molecules in solution and in PDI films.[1] For no-PDI aggregate formation is much less probable, because the bay groups prevent from an effective overlap of the PDI electronic wave functions. Nevertheless, diffusion data are for both types of molecules qualitatively very much similar for both types of molecules.

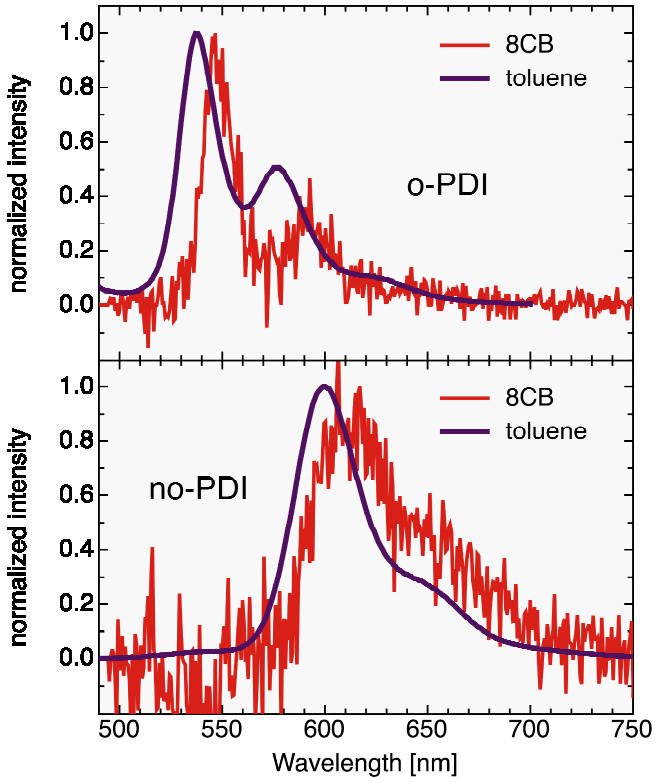

Figure S1: Normalized fluorescence spectra of single o-PDI molecules in 8CB (top) and no-PDI in 8CB (bottom). For comparison ensemble spectra of o-PDI and no-PDI are shown in toluene solvent. Excitation wavelength is in all cases 488 nm. Single molecule spectra have been obtained via a confocal microscope in a 225 nm thick film on 16 nm thick SiO_2. Due to the very thin SiO_2 layer on the Si substrate the fluorescence of PDI molecules close to the SiO_2 interface is quenched.

To characterize a possible alignment of PDI dye molecules in liquid crystal films, we investigated the fluorescence in a twisted nematic liquid crystal cell. It has been shown recently, that dye molecules align with respect to the order parameter of the liquid crystal.[2,3] Applying an external voltage to the cell changes the fluorescence intensity of the dye as long

as the dye has a pronounced optical polarisation. The optical absorption and emission of PDI dyes is nearly completely polarized along the long molecular axis even if bay groups are present.[4]

We have built a liquid crystal cell consisting of 2 glass substrates covered by ITO and a surface structured polymer (polyimide 150 NC) to apply an external voltage up to 20 V and to guarantee the orientation of nematic layers close to the interface. The structure of the polymer at the two opposite cell walls has been oriented perpendicular to each other to establish an orientation of the nematic layers rotated by 90°. The separation between the two oriented cover glasses is ~ 13 μm. To demonstrate orientation effects for PBI we have used 5CB instead of 8CB, since at room temperature 5CB is in its nematic phase in contrary to 8CB which is smectic at this temperature. The concentration of PDI dyes in 5CB is close to 10^{-6} mol/l.

All optical experiments have been performed with 488 nm excitation from a laser scanning microscope (Zeiss) and a direction of observation perpendicular to the liquid crystal cell. For detection either the microscope or a monochromator, which has been coupled via an optical fiber, have been used. Figure S2 shows the fluorescence spectra of o-PDI and no-PDI in toluene and in 5CB. It is obvious that the general shape of the spectra is maintained in 5CB as compared to toluene in each case, but the spectra are shifted to the red by about 10 nm. We attribute these shifts to solvent effects via the increase of the dielectric constant ε when proceeding from toluene to 5CB. In 5CB the o-PDI dye shows some additional structure which either stems from aggregate formation or from conformations. Similar effects have been observed for related PDI dyes.[3] Even if some aggregate formation might take place, this is further suppressed at the low concentrations used in our single molecule diffusion experiments, where extensive fluorescence blinking has been observed. Moreover, diffusion of (single) aggregates merely changes the absolute magnitude of the diffusion coefficient by a factor of about 2, but can not explain the wide distribution of diffusion dynamics observed in the reported experiments.

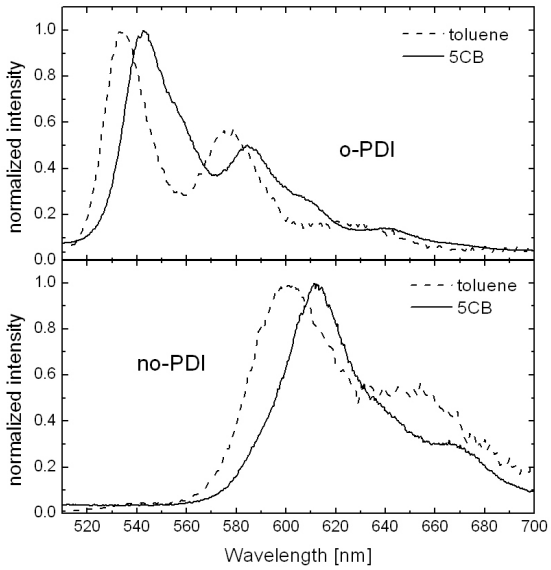

Figure S2: Normalized fluorescence spectra of PDI in toluene (broken line) and 5CB (full line) for o-PDI (top) and no-PDI (bottom) at excitation wavelength of 488 nm.

Figure S3 shows the fluorescence intensities of PDI dyes as a function of the applied voltage. The inset shows the spectra of o-PDI at 0 V and 15 V respectively. No change in the spectral

shape is observed upon voltage increment. However, the overall fluorescence intensity of o-PDI is decreased by about 88 % while the one of no-PDI is only changed by about 8 % at 20 V. For o-PDI this value is in agreement with the intensity ratios reported for other aligning dye molecules.[2] While o-PDI shows a continuous decrease with increasing voltage, no-PDI exhibits a decrease by 20 % below 5V which is diminished again on further increasing the voltage. We did not follow these phenomena as our basic interest was to see whether the switching of the liquid crystal cell (which was independent of the guest molecules) influences the alignment of the PDI dye molecules. From Figure S3 it is evident, that o-PDI is much more influenced than no-PDI. At an external voltage of V=0 the cell is in transmission mode as the twisted director field turns the direction of polarization of the light so that it can pass the crossed polarisers. In case that PDI is oriented with its optical transition moment (which is along the long molecular axis) parallel to the director it can absorb and emit light perpendicular to the interface. When switching the cell (at V = 20 V) the liquid crystal director aligns perpendicular to the interface and co-aligned PDI dyes can no longer absorb and emit light, which obviously applies only for o-PDI.

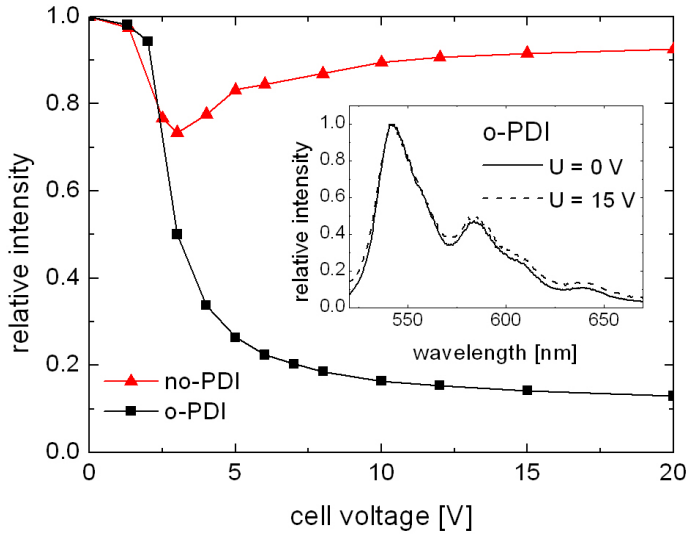

Figure S3: Relative fluorescence intensities of o-PDI (squares) and no-PDI (triangles) as a function of cell voltage. The inset shows the fluorescence intensity of o-PDI for two voltages. Excitation wavelength 488nm.

From the intensity change we determine an "order" parameter S_V of PDI with respect to the one of 5CB according to

$$S_V = \frac{I_o - I_V}{I_o + 2I_V},$$

where I_o and I_V apply to the fluorescence intensity at V = 0 and variable V, respectively. For o-PDI this results in $S_V \approx 0.7$ at 20 V and for no-PDI in $S_V \approx 0.1$ at 5 V and $S_V \approx 0.04$ at 20 V. Since we did not determine the absolute value of the orders parameter for the liquid crystal director, the given values S_V are only upper limits. Nevertheless they show a pronounced dependence on the kind of dye molecule, from which we safely conclude that o-PDI follows the orientation of the 5CB director considerably stronger than no-PDI. From geometric arguments this should also apply to the nematic phase of 8CB. Since o-PDI is only slightly longer than the diameter of a smectic 8CB double layer, preferred orientation of o-PDI should also be observed in this case.

The missing ordering of no-PDI is at first glance somewhat surprising, since it might show a similar preferred orientation, but in this case along its short in-plane axis. However, taking the out-of-plane positions of the bay groups into account, the overall shape of no-PDI resembles more closely a sphere. Moreover, the bay groups impose various conformations[4], which shows up e.g. in the rather blurred fluorescence spectra (see Figure S1 and Figure S2).

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