Field controlled charge-separation in a conductive matrix at the single molecule level: towards controlling single molecule fluorescence intermittency.

Koen Kennes, Peter Dedecker, James A. Hutchison, Eduard Fron, Hiroshi Uji-i, Johan Hofkens, Mark Van der Auweraer

Molecular Imaging and Photonics, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.

ISIS & icFRC, University of Strasbourg & CNRS UMR 7006, 8 allée Gaspard Monge, Strasbourg 67000, France.

School of Chemistry and Bio21 Institute, University of Melbourne, Victoria 3010, Australia.

RIES, Hokkaido University, N20W10, Kita-Ward Sapporo 001-0020 Japan.

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Supporting information

Figure S1. An example of a trace of ATTO647N in a polystyrene matrix. No influence on the fluorescence intensity was detected. 20 molecules tested.

Using the binning and thresholding method the on and off times can be calculated for each individual event i.e. intensity change, both when the electric field is turned on and off. Both for traces collected in the presence and absence of an electric field all on/off times of all events in one trace can be added to obtain the average on/off time. This allows us to compare the histograms of the on and off times with and without an electric field.
Figure S2. Histogram of the on and off time histograms in the presence and absence of an electric field of a typical molecule that shows reduced fluorescence intensity in the presence of an electric field. The average value of the on and off times in the absence and presence of an electric field: 20.3 ms, $t_{on}(0V)$: 19.5 ms, $t_{off}(0V)$: 2.3 ms, $t_{off}(20V)$: 8 ms. Information from all on-off cycles was combined to construct the histograms.

The histograms of the on and off times of one single molecule, both with and without electric field, closely resemble mono exponentials which after fitting give the average on or off time. Figure S1 displays these histograms for the trace in Figure 2B. In this specific case, where the fluorescence is being suppressed by the electric field, the off times become significantly longer upon applying an electric field while for the on times the observed increase is less than 10%. Furthermore a significant contribution of very long on times can be observed in the presence of an electric field. However one should take into account that, due to the limited amount of data in the histogram of a single molecule, it will be difficult to discriminate between an exponential distribution and a distribution governed by an inverse power law. Unless one very stable molecule is encountered it is, as reported in the literature, difficult to observe these power laws unambiguously. Since for the data shown in Figure S1 we are enhancing the charge separation which mainly results in a longer presence of the reactive radical anion of ATTO, as indicated by the longer off times, the application of the electric field will enhance the photo bleaching and we can expect that the observed survival time of the dye (i.e. the time until bleaching) in the PVK-matrix becomes shorter upon application of an electric field. Therefore we made global histograms including the traces of all molecules that showed a similar response (i.e. decrease of intensity) to the electric field. This approach allowed us to attain a signal to noise ratio that was sufficient to fit the observed data to an inverse power law.

Figure S2 shows that it is indeed possible to fit the overall distribution of the off times to an inverse power law with an exponent of $2.5\pm0.09$ and $2.4\pm0.09$ respectively in the absence and presence of an electric field (by combining the off times of all molecules showing a decreased intensity in the presence of an electric field). When the on times of all molecules showing a decreased intensity in the presence of an electric field are combined a power law is followed at long time scales (i.e. on times beyond 25 μs), both in the presence and in the absence of an electric field. Fitting the on times above 25 μs yields power laws with exponent $\mu \sim 1.9$ both in the absence and presence of an electric field. However at short times an exponential cutoff has to be taken into account in both cases. It could be possible that due to the on times in general being longer than the off times more data points are needed to obtain a full power law. Another possible cause could be the broader range of rate constants for charge recombination compared to charge separation leading to an exponential distribution for the short on times.
Figure S3. Ensemble histograms of the off (A) and on (B) times on a log-log scale. These histograms were constructed by combining all data (on times or off times) of all molecules giving a decreased intensity in the presence of the applied field. The lines indicate the fits.

In order to get more insight into the effect of the electric field on the on and off times we compared the on and off times of every single molecule for every cycle. In order to do this accurately a large number of events are needed per cycle. When attempting to analyze these data by the binning and thresholding method one has to be aware that this approach is to some extent subjective as binning time and threshold are chosen by the experimenter. Therefore the reliability of this approach has been matter of debate.\textsuperscript{2,47} Considering the limited number of events per cycle it can be more advantageous to determine the average on and off time for every cycle using the autocorrelation method.

**Cyclic voltammetry** was used to determine the oxidation and reduction potential of ATTO647N. The electrochemical measurements were carried out in a custom made single compartment three-electrode cell with a working volume of 1 cm\(^3\), containing a Pt coil counter electrode. The reference electrode was a lab-built non-aqueous Ag—Ag\(^+\) electrode, contacted to the cell through a porous glass diaphragm, and was calibrated versus ferrocene after the measurements. All potentials are given with reference to the ferrocene equilibrium potential. The working electrode (WE) was a polycrystalline Pt bead, polished to mirror finish, exposing a geometric surface area of 0.032 cm\(^2\) in a hanging meniscus configuration. The WE was butane flame annealed before every measurement, and cooled down in a stream of high purity Ar. The potentiostat was a computer controlled Autolab PGSTAT101 system (Metrohm Autolab BV, The Netherlands). In all cases, the WE was brought into contact with the electrolyte under potential control, at a potential value within the stability range of the studied compound. The solution in acetonitrile had a concentration of 1 mM and contained 0.1 M TBAPF\(_6\) as supporting electrolyte. \(E_{\text{ox}} = 0.44\) V and \(E_{\text{red}} = -1.25\) V.
Figure S4. Cyclic voltammogram of ATTO647N in acetonitrile at 1 mM concentration. Supporting electrolyte TBAPF$_6$ 0.1 M; scan rate 50 mV s$^{-1}$. The black dashed trace shows the base electrolyte response.

**Time of flight experiments.** A nitrogen laser (Model VSL-337ND-S, Spectra-Physics) was employed as an excitation source for the time-of-flight experiments and yielded 337 nm light pulses with a duration of 4 ns. Excitation occurred through the positive top electrode (thin Al electrode) and the current transient was measured between the bottom electrode (thick aluminum electrode) and the ground with a LeCroy 9400A digital oscilloscope triggered by the laser pulse. The load resistance used for each measurement was chosen to obtain a resistance-capacitance time (tRC) of the measurement circuit that was at least 50 times shorter than the expected values of the transit time ($t_t$) of the charge carriers. The excitation intensity was controlled by two polarizers. The sample was mounted in a vacuum chamber with a quartz window. The temperature in the vacuum chamber was regulated by using a flow water thermostat connected to the (hollow) back wall of the chamber. The temperature of the sample was measured by a thermocouple with an accuracy of 0.5 K. The transit time ($t_t$) was determined from the intersection point of the two asymptotes to the traces in a double logarithmic plot of the transient photocurrent. The hole mobility can then be determined through:

$$\mu = \frac{d}{t_t E}$$

where $\mu$ is in this case a drift mobility of the holes (cm$^2$ V$^{-1}$ s$^{-1}$), d is the thickness of the organic film (cm), and E is the applied electric field (V cm$^{-1}$). According to the Pool-Frenkel formalism:

$$\ln(\mu) = \ln(\mu_0) + S\sqrt{E}$$

where $\mu_0$ corresponds to the experimental mobility extrapolated to zero field and S is a slope of the Poole-Frenkel plot. As shown in figure S4, the field dependence of the hole mobility in PVK at 298K could be fitted to Poole-Frenkel formalism for temperatures between 298 K and 348 K.

Figure S5. Pool-Frenkel plots for the hole mobility in PVK at different temperatures.
According to the Bässler Gaussian disorder model\textsuperscript{53} the field and temperature dependence of the mobility should correspond to the relation:

$$\mu = \mu_{00} e^{\exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right]} e^{\exp\left[E^{1/2}C\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right]}$$

where $\mu_{00}$ corresponds to the mobility extrapolated to zero field and infinite temperature, $\sigma$ is the energetic disorder parameter corresponding to the standard deviation of density of states of the transport levels (which is assumed to be a Gaussian), $\Sigma$ is the positional disorder parameter describing the fluctuation of intersite distances and coupling between the transport sites, and $C$ is an empirical constant. The following plots allow for the determination of $\sigma$, $\Sigma$ and $C$.

\begin{align*}
\ln(\mu_0) &= \ln(\mu_{00}) - \left(\frac{2\sigma}{3kT}\right)^2 \\
S &= \frac{\delta \ln(\mu)}{\delta \sqrt{E}} = C\left(\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right)
\end{align*}

Figure S6. Plot of the logarithm of zero field mobility ($\ln(\mu_0)$) against $(1000/T)^2$ (upper plot) and plot of the Poole-Frenkel slope ($S$) against $(\sigma/kT)^2$ (lower plot).

|   | ln($\mu_{00}$) (cm$^2$/Vs) | $\sigma$ (meV) | $\Sigma$ | $C(x10^{-5})$ |
|---|--------------------------|---------------|---------|---------------|
| PVK | -7.28                    | 129           | 7.6     | 5.5           |

Table S1. Parameters for hole transport in pristine PVK films obtained from the Bässler model.

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