Supplementary information: Addressing single spin-crossover molecules in a two-dimensional monolayer

Yongfeng Tong,[1] Massine Kelaï,[1] Kaushik Bairagi,[1,*] Vincent Repain,[1] Jérôme Lagoute,[1] Yann Girard,[1] Sylvie Rousset,[1] Marie-Laure Boillot,[2] Talal Mallah,[2] Cristian Enachescu,[3] and Amandine Bellec[1,†]

[1] *Université de Paris, Laboratoire Matériaux et Phénomènes Quantiques, CNRS, F-75013, Paris, France*
[2] *Institut de Chimie Moléculaire et des Matériaux d'Orsay, Universiteé Paris-Saclay, CNRS, UMR 8182, 91405 Orsay 12 Cedex, France*
[3] *Faculty of Physics, Alexandru Ioan Cuza University of Iasi, Iasi 700506, Romania*

* present address:Université Grenoble Alpes, CEA, CNRS, Grenoble INP, IRIG-SPINTEC, 38054 Grenoble, France
† amandine.bellec@univ-paris-diderot.fr

A. Molecular structure on Cu(111)

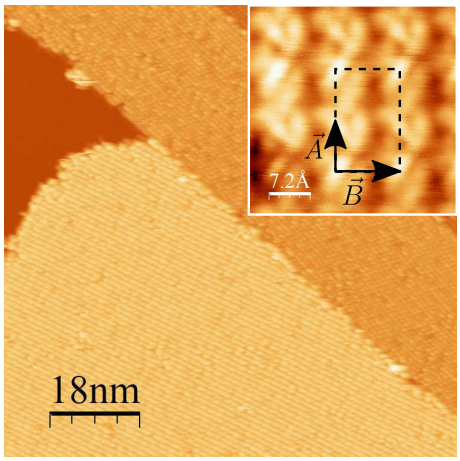

FIG. S1. 90×90 nm^2 STM topographic image with molecular islands ($V = -1.5$ V, $I = 50$ pA). Inset, 3.6×3.6 nm^2 zoom with intra-molecular resolution ($V = -2.5$ V, $I = 50$ pA). The vectors between neighbour molecules and the molecular lattice cell are schematized by the arrows and the rectangle, respectively.

Figure S1 presents the molecular islands grown on Cu(111). The measured distance between neighbour molecules are $\left\|\vec{A}\right\| = 8.7 \pm 0.1$Å, $\left\|\vec{B}\right\| = 10.5 \pm 0.1$Å and $(\vec{A}, \vec{B}) = 90 \pm 3°$ (the error bars correspond to the standard deviation). Along $\vec{A}$, two orientations of the molecules are observed leading to a primitive molecular cell containing two molecules as shown in the inset of Figure S1. On the Au(111) substrate, the molecular network has similar lattice vector norms ($\left\|\vec{A}\right\| = 8.6 \pm 0.2$Å, $\left\|\vec{B}\right\| = 10.6 \pm 0.3$Å) than the vector norms between two neighbour molecules but different lattice angle ($(\vec{A}, \vec{B}) = 80 \pm 2°$) [1, 2].

B. Molecular superstructure on Au(111)

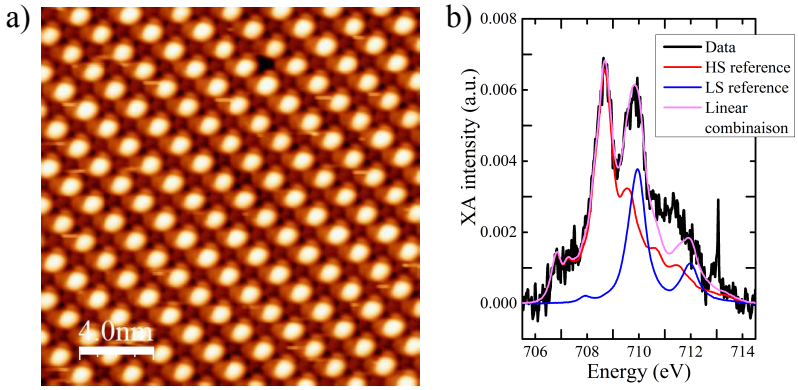

FIG. S2. a) 20×20 nm^2 topographic image of FeMPz on Au(111) at a bias voltage of 0.3 V (I= 200 pA). b) Average XAS spectrum (over 5 spectra) at the Fe L_3 edge recorded at 80 K on 0.8±0.1 ML of FeMPz on Au(111) (black curve). The reference spectra of the LS (blue) and HS (red) states along with their linear combinaison (pink) are superimposed. For this curve, the HS proportion is 67%.

As shown in Figure S2.a, we observed on Au(111) at 0.3 V a robust long-range superstructure with one bright molecule for two dark molecules [1]. The bright molecule was first wrongly assigned to the high spin state of the

molecules [1]. Indeed, x-ray absorption spectroscopy measurements (Figure S2.b) realized on four different samples clearly indicate that at low temperature two third of the molecules are in the high spin state and one third are in the low spin state [3].

C. Moran index on the thermal states

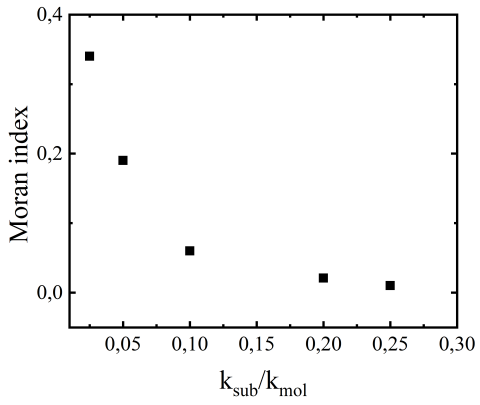

FIG. S3. Moran index determined after relaxation for different k_{sub}/k_{mol} values.

To evaluate the spatial correlations between the molecules in the different states, we use the Moran index. Its general definition is:

$$I_{Moran} = \frac{N}{W} \frac{\Sigma_i \Sigma_j w_{ij}(x_i - \bar{x})(x_j - \bar{x})}{\Sigma_i (x_i - \bar{x})^2}$$

where N is the total number of molecules, x codes for the spin state of the molecules (1 for HS molecules and -1 for LS molecules), w_{ij} is the weight of every (i, j) pairs and $W = \Sigma_{i,j} w_{i,j}$. We restricted the estimated Moran index to the molecules that are first neighbours, so for a molecule i, $w_{ij} = 1$ if the j^{th} molecule is a first neighbour of i else $w_{ij} = 0$. A value of 1 corresponds to a perfectly correlated system with large clusters of molecules in the same spin state. A value of 0 indicates the absence of correlation with a disordered mixture of molecules in HS and LS states. Finally, a value of -1 corresponds to a anti-correlated system with a perfect alternating of molecules in LS and HS states.

Figure S3 compares the Moran indexes determined for the stationary state as a function of k_{sub}/k_{mol}. The Moran index decreases to zero, *i.e.* no correlation between the spin states of the molecules, when k_{sub} increases. As a comparison, experimentally we measured a Moran index around 0.2 on Cu(111) both for the thermal and the photoexcited states. For Au(111), long-range super-structure where one molecule is in LS state for two in HS state is measured. The Moran index can thus be calculated and is equal to -0.5, indicating anti-correlation interactions between the molecules.

D. Voltage pulses on Au(111)

Figures S4.a to c present consecutive STM images of the initial state, the defect creation and its relaxation for the example given in the main text. The schematic in Figure S4.d represents the molecular network on which the circles highlight the bright molecules of the initial superstructure (in red) and of the created four-bright-molecule defect (in blue). One can observe the commensurability between the four-bright-molecule defect and the superstructure. It can be noted that this defect is also commensurate with the photoexcited phase described in 1. The same type of defects are also observed in Figure S4.e after a larger voltage pulse (2.2 V).

For each image of the series presented in Figure S5 (see also in the main text), the area (A) of the phase-shifted domain is estimated. By approximating the inner domain by a circle, an effective radius (R_{eff}) is defined as $R_{eff} = \sqrt{A/\pi}$. The evolution of the effective radius as a function of time is plotted in Figure S5.f (squares). In the theory of Ostwald ripening, the evolution with time of the effective radius is expected to follow the equation $R_{eff}^3 = R_0^3 - \alpha t$ with R_0

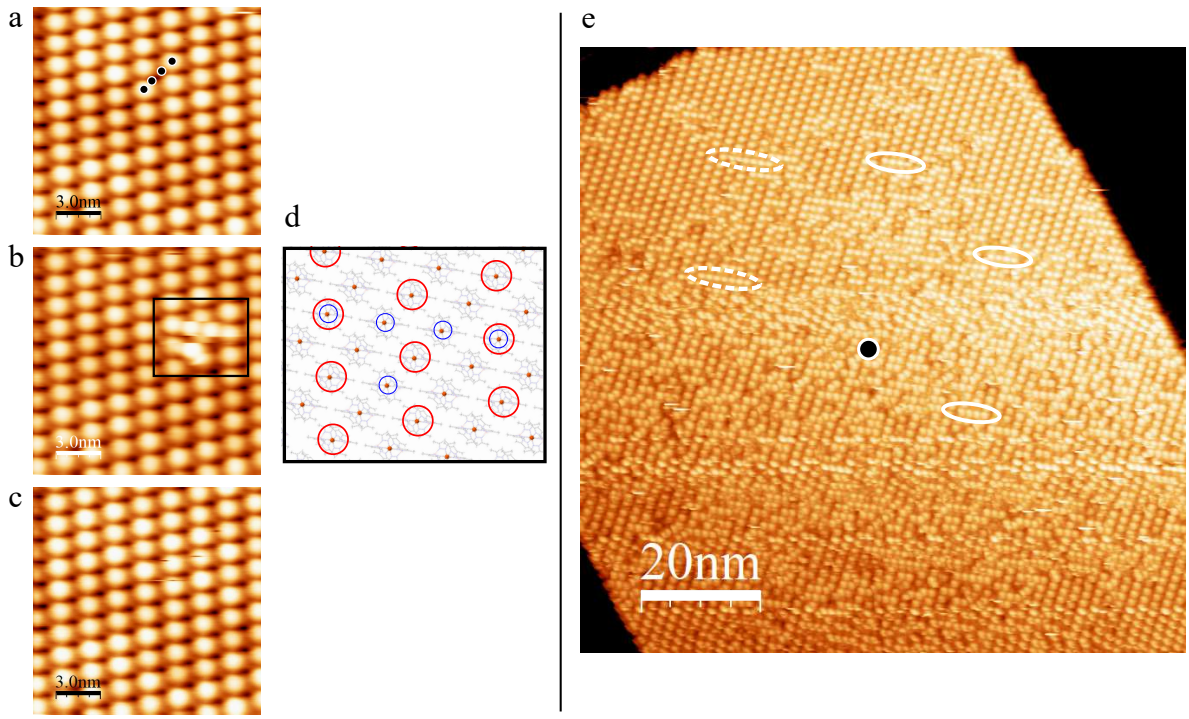

FIG. S4. a) to c) 15×15 nm^2 consecutive STM topographic image acquired after the application of four voltage pulses at 0.6 V on the different application points marked by the black dots in a ($V = 0.3$ V, $I = 20$ pA). d) Schematic of the 4-bright-molecule defect in b. The full molecular network is represented. The red circles indicate the bright molecules of the thermal state and the blue circles indicate the bright molecules of the created defect. 100×100 nm^2 e) STM topographic image of a molecular island after a voltage pulse at 4.0 V (10 ms) applied at the location of the black dot ($V = 0.3$ V, $I = 10$ pA). The circles in solid line and dotted line highlight some four-bright-molecule and seven-bright-molecule defects, respectively.

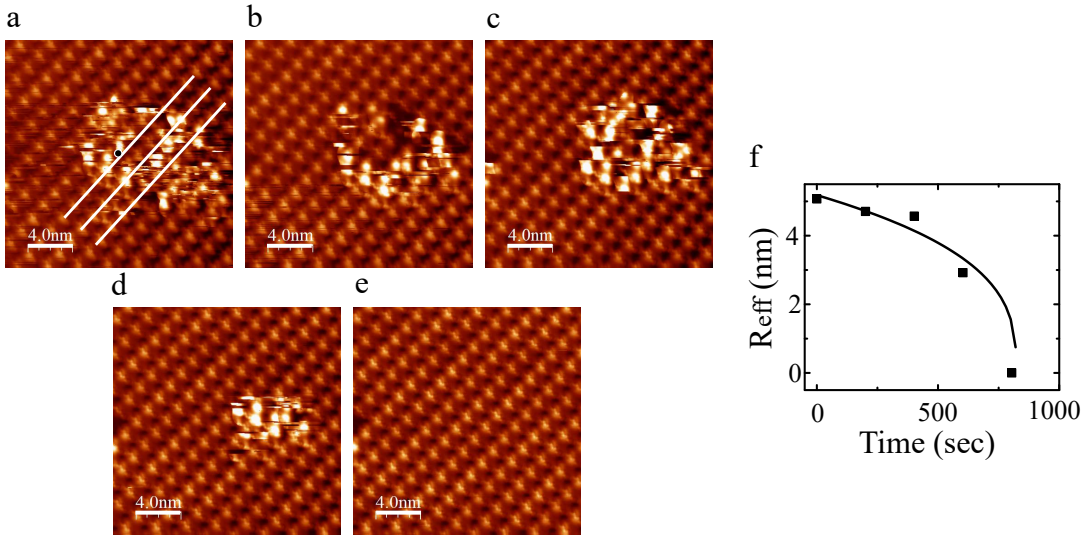

FIG. S5. a) to e) Consecutive 20×20 nm^2 STM current images after a voltage pulse at 2.2 V (10 ms) applied at the location of the black dot ($V = 0.3$ V, $< I >= 10$ pA) in a). The white lines are aligned along the dense direction of the outer superstructure to highlight the phase shift in the inner domain. b) to e) consecutive STM images showing the shrinking of the inner domain. f) Effective radius of the inner domain (R_{eff}) as a function of time (black squares). The solid line corresponds to a simulation in the framework of Ostwald ripening theory.

the initial radius and α a proportionality factor [4]. In Figure S5.f, the solid line is obtained for $R_0 = 5.2$ nm and $\alpha = 0.17$ nm^3.s^{-1}.

E. Stability of the molecular state under scanning on Cu(111)

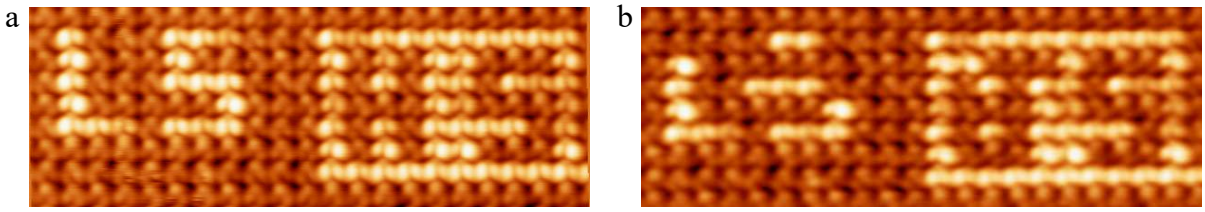

FIG. S6. Evolution of the written "LS" and "HS" with time. The area has been scanned at 0.3 V for 13 hours. 7.8×22.1 nm^2 STM topographic image a) of LS and HS after the writing and b) after 13 hours of scanning at 0.3 V. Both images have been recorded at $V = 0.3$ V and $I = 3$ pA. Few defects have appeared in the written "LS" and "HS".

F. Environment effect on the switching probability

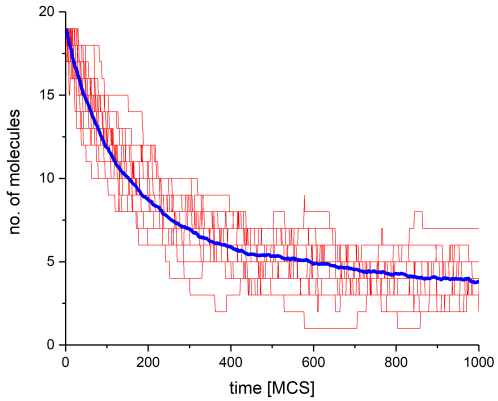

FIG. S7. In red, twenty (out of the hundred) curves simulated for the relaxation of a cluster of HS molecules in a LS environment with k_{sub}/k_{mol}=0.05. The blue curve corresponds to the average over the hundred simulated curves shown in the main text.

G. Creation of a dark area: switching from LS to HS by voltage

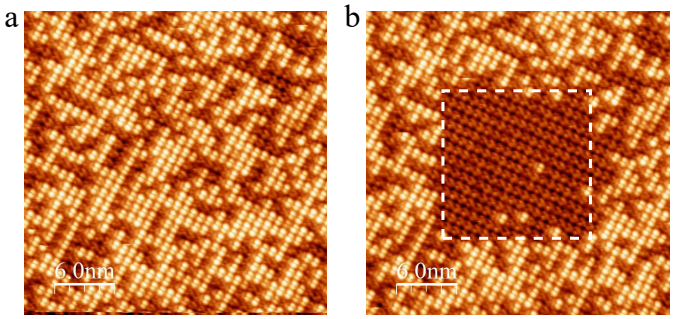

FIG. S8. Creation of a dark area by scanning at 0.7 V. 30×30 nm^2 STM topographic images of a) the initial obtained after blue light photoexcitation and b) after the scan of a central 15× 15 nm^2 area at 0.7 V (schematized by the white square). Both STM topographies have been acquired at $V = 0.3$ V and $I = 20$ pA.

H. Analysis of the $I(t)$-traces and yield determination

To determine the switching yield, we analysed current-versus-time traces recorded in two environments, i.e. the $I(t)$-traces recorded over a molecule surrounded by dark or by bright neighbours. The analysis procedure is summarized in Figure S9. The STM images present for both environments an example of the initial (Figure S9.a and f) and final (Figure S9.b and g) states with the corresponding I(t)-traces recorded during the voltage pulse (in blue in the Figure S9.c and h). All the experimental $I(t)$-traces are analysed by a home-made program to define the upper ($I_{LS\rightarrow HS}$) and lower ($I_{HS\rightarrow LS}$) tunneling currents along with the duration of upper ($\Delta t_{LS\rightarrow HS}$) and lower ($\Delta t_{HS\rightarrow LS}$) plateau. From these values, the ideal traces fitting the experimental ones are plotted (see orange curves in Figure S9.c and h) and the $I \times \Delta t$ distributions are deduced (blue points in Figure S9.d, e, i and j). The distributions are fitted by an exponential decay enabling the determination of the characteristic $I \times \Delta t$ values to calculate the yield. All the values are summarized in the table I. The series presented here were realized for a given tip state. Similar yield values were obtained for other tip states.

	bright to dark ($LS \rightarrow HS$)		dark to bright ($HS \rightarrow LS$)	
	$I_{LS\rightarrow HS} \times \Delta t_{LS\rightarrow HS}$	$Y_{LS\rightarrow HS}$	$I_{HS\rightarrow LS} \times \Delta t_{HS\rightarrow LS}$	$Y_{HS\rightarrow LS}$
Dark neighbours	4.10 pA.s	3.9 10^{-8}	2.90 pA.s	5.5 10^{-8}
Bright neighbours	12.74 pA.s	1.3 10^{-8}	0.86 pA.s	18.6 10^{-8}

TABLE I. Characteristic $I \times \Delta t$ and switching yields for the bright to dark ($LS \rightarrow HS$) and dark to bright ($HS \rightarrow LS$) switching depending of the molecule environment.

[1] K. Bairagi, O. Iasco, A. Bellec, A. Kartsev, D. Li, J. Lagoute, C. Chacon, Y. Girard, S. Rousset, F. Miserque, Y. J. Dappe, A. Smogunov, C. Barreteau, M.-L. Boillot, T. Mallah, and V. Repain, Nature Communications **7**, 12212 (2016).
[2] C. Fourmental, S. Mondal, R. Banerjee, A. Bellec, Y. Garreau, A. Coati, C. Chacon, Y. Girard, J. Lagoute, S. Rousset, M.-L. Boillot, T. Mallah, C. Enachescu, C. Barreteau, Y. J. Dappe, A. Smogunov, S. Narasimhan, and V. Repain, The Journal of Physical Chemistry Letters **10**, 4103 (2019).
[3] L. Zhang, Y. Tong, M. Kelai, A. Bellec, J. Lagoute, C. Chacon, Y. Girard, S. Rousset, M.-L. Boillot, E. Rivière, T. Mallah, E. Otero, M.-A. Arrio, P. Sainctavit, and V. Repain, Angewandte Chemie International Edition **59**, 13341 (2020).
[4] K. Morgenstern, G. Rosenfeld, and G. Comsa, Physical review letters **76**, 2113 (1996).

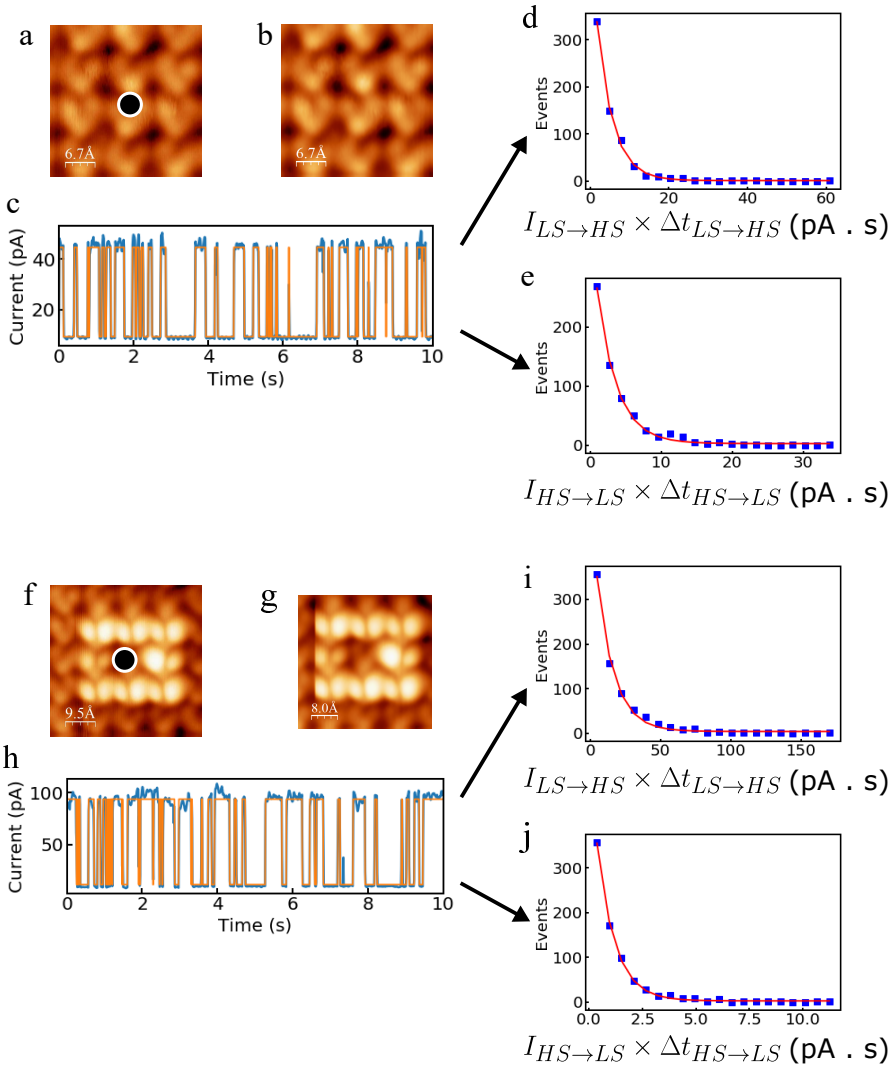

FIG. S9. Determination of the switching yields for a molecule surrounded by dark (HS) neighbours (a-e) or by bright (LS) neighbours (f-j). STM topographic images a) before and b) after a voltage pulse of 0.5 V ($V = 0.3$ V, $I = 5$ pA). In a) the position of the tip during the voltage pulse is schematized by a black dot. c) $I(t)$-trace recorded during the voltage pulse in blue and compared to the ideal trace determined by our home-made program in orange. Distribution of d) $I_{LS\rightarrow HS} \times \Delta t_{LS\rightarrow HS}$ and e) $I_{HS\rightarrow LS} \times \Delta t_{HS\rightarrow LS}$ when the switched molecule is surrounded by dark molecules. The blue squares correspond to the measured distributions and the red line to the exponential fits. STM topographic images f) before and g) after a voltage pulse of 0.5 V ($V = 0.3$ V, $I = 5$ pA) In f) the position of the tip during the voltage pulse is schematized by a black dot. h) $I(t)$-trace recorded during the voltage pulse in blue and compared to the ideal trace determined by our home-made program in orange. Distribution of i) $I_{LS\rightarrow HS} \times \Delta t_{LS\rightarrow HS}$ and j) $I_{HS\rightarrow LS} \times \Delta t_{HS\rightarrow Ls}$ when the switched molecule is surrounded by bright molecules. The blue squares correspond to the measured distributions and the red line to the exponential fits.