Conductance switching at the nanoscale of diarylethene

derivatives self-assembled monolayers on

$La_{0.7}Sr_{0.3}MnO_3$

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Supporting information

Synthesis of dithienylethene diphosphonic acid (DDA).

Dibromide **1** then diphosphonate **2** precursors were prepared according to the method of Feringa et al.¹ We followed the method of Reisinger et al.² to synthesize the dithienylethene diphosphonic acid (DDA).



Reaction was performed under an inert atmosphere in oven-dried glassware and protected from UV light. A solution of diphosphonate 2 (250 mg, 0.36 mmol) in dry acetonitrile (20 mL) was treated with trimethylsilyl bromide (0.75 mL, 4.6 mmol). The mixture was stirred overnight at room temperature under nitrogen. Volatile compounds were removed under vacuum then 20 mL of methanol was added then the solution was stirred overnight. After evaporation of the solvent, the residue was kept at 60°C/0.1 mbar for 3 h to remove traces of solvents and silylated compounds. A control by TLC on SiO₂ (AcOEt/hexane 95:5) of the obtained yellow oil indicated the total disappearance of diphosphonate 2. Addition of CH2Cl2 to the oil provided DDA as a thin white solid that was isolated by centrifugation (177 mg, 84%). DDA was purified by additional cleaning with CH₂Cl₂, centrifugation then drying under vacuum. Yield: 84 %. ¹H NMR δ (300.13 MHz, CD₃OD): 1.99 (6H, s, thiophene-CH₃), 2.10 (2H, quint, J = 7.4 Hz, cyclopentene-CH₂), 2.85 (4H, t, J = 7.4 Hz, cyclopentene-CH₂), 7.16 (2H, s, thiophene-H), 7.40-7.46 (2H, m, phenyl-H), 7.61-7.68 (4H, m, phenyl-H), 7.94 (2H, d, J = 14.2 Hz, phenyl-H). ¹³C {¹H, ³¹P} NMR δ (100.67 MHz, d6-DMSO) : 14.06, 22.41, 38.06, 124.79, 126.78, 127.21, 129.02, 129.25, 133.45, 134.18, 134.31, 135.02, 136.85, 138.30. ³¹P {¹H} NMR δ (162.05 MHz, d6-DMSO) : 12.94. NSI-HRMS: m/z [M+H]⁺ calcd. for C₂₇H₂₆O₆P₂S₂: 573.07188, found : 573.07134.

NMR spectra of DDA :





HRMS spectrum :





Figure S1. (a) UV-vis absorption of DDA in ethanol: reference before irradiation (black line), after irradiation at 365 nm for 2 min (red line), for 5 min (blue line) and after irradiation 15 min in visible (pink line). The peak at 530 nm is the fingerprint of the DDA-c form. Inset : solution before (left) and after the 365 nm irradiation (right). (b) Reversible switching of the absorbance at 530 nm (main peak) under several cycles of UV and visible light irradiations. Note that we tried a similar UV-vis experiment on the DDA SAM on LSMO. Albeit we can observe a very small peak at around 530 nm, the signal was too weak (about 10⁻³ with respect to the LSMO contribution) to resolve any signature of the DDA switching.

Ellipsometry.

We recorded spectroscopic ellipsometry data in the visible range using an UVISEL (Jobin Yvon Horiba) spectroscopic ellipsometer equipped with DeltaPsi 2 data analysis software. The system acquired a spectrum ranging from 2 to 4.5 eV (corresponding to 300 to 750 nm) with intervals of 0.1 eV (or 15 nm). Data were taken at an angle of incidence of 70°, and the compensator was set at 45°. Data were fitted by a regression analysis to a film-on-substrate model as described by their thickness and their complex refractive indexes. First, a background for the LSMO substrate before monolayer deposition was recorded. Secondly, after the monolayer deposition, we used a 2-layer model (substrate/SAM) to fit the measured data and to determine the SAM thickness. We employed the previously measured optical properties of the LSMO substrate (background), and we fixed the refractive index of the organic monolayer at 1.50. The usual values in the literature for the refractive index of organic monolayers are in the range 1.45–1.50.³ We can notice that a change from 1.50 to 1.55 would result in less than 1 Å error for a thickness less than 30 Å. We estimated the accuracy of the SAM thickness measurements at ± 2 Å.

Contact angle measurements.

We measured the water contact angle with a remote-computer controlled goniometer system (DIGIDROP by GBX, France). We deposited a drop (10-30 μ L) of deionized water (18M Ω .cm⁻¹) on the surface and the projected image was acquired and stored by the computer. Contact angles were extracted by a contrast contour image analysis software. These angles were determined few seconds after the application of the drop. These measurements were carried out in a clean room (ISO 6) where the relative humidity (50%) and the temperature (22°C) are controlled. The precision with these measurements are ± 2°.

XPS.

XPS was performed with a Physical Electronics 5600 spectrometer fitted in an UHV chamber with a residual pressure of 2×10^{-10} Torr. High resolution spectra were recorded with a monochromatic Al K α X-ray source (h ν = 1486.6 eV), a detection angle of 45° as referenced to the sample surface, an analyzer entrance slit width of 400 µm and with an analyzer pass energy of 12 eV. Semi-quantitative analysis was completed after standard background subtraction according to Shirley's method.⁴ Peaks were decomposed by using Voigt functions.

AFM and C-AFM.

Atomic force microscopy (topography) and conducting atomic force microscopy (C-AFM) were performed in air (of under a flux of dry N_2) (ICON, Bruker), using a tip probe in platinum/iridium or platinum. The tip loading force on the surface was to 30 nN. Albeit larger than the usual loading force (2-5 nN) used for C-AFM on SAMs, this value is below the limit of about 60-70 nN at which the SAMs start

to suffer from severe degradations. For example, a detailed study (Ref. 5) showed a limited strain-induced deformation of the monolayer (≤ 0.3 nm). The same conclusion was confirmed by our own study comparing mechanical and electrical properties of alkylthiol SAMs on flat Au surfaces and tiny Au nanodots.⁶ In addition, we note that imaging several times the same area of the SAMs (e.g. as in Figs. 3c, 4c) showed no significant degradation of the SAMs. We have also chosen this value of the loading force, since the currents on the DDA/LSMO SAMs are low and would not be measured (or only a much weaker number, thus degrading the statistical analysis) using a weaker loading force. The topographic and current images are recorded simultaneously. To measure the current-voltage (I-V) curves and the current histograms, a square grid of 10×10 or 20x20 was defined with a pitch of 50 or 100 nm. At each point, the I-V curve is acquired leading to the measurements of 100 or 400 I-V traces per grid. This process was repeated several times at different places on the sample, and up to thousands of I-V traces were used to construct the current-voltage histograms. The bias was applied on the LSMO substrate and the tip was grounded through the input of the current amplifier. Note that around 0V the currents are very weak and in many cases at the limit of detection (0.1 pA).

C-AFM in UHV (10-9 - 10-11 mbar) was performed using a VT-SPM (Variable temperature scanning probe microscope, Scienta Omicron) using a PtIr coated

tip (SCM-PIC-V2). The tip loading force was set to 30 nN. Current-voltage spectroscopy was performed on 20×20 grids with a pitch of 100 nm. Grids were spaced a few mm away from each other. Under UHV, the bias was applied on the probe and the sample was grounded.

UV-vis irradiations.

For the light exposures, an optical fiber, with a 400 µm diameter, was brought near the samples. We used 2 power LED from Thorlabs, with the following characteristics: i) 365 nm, bandwidth of 10 nm, for the open-to-closed isomerization, ii) 470 nm, bandwidth of 20 nm, for the close-to-open isomerization. The light power values were measured with a calibrated Optical Power and Energy meter PM200 (Thorlabs). They were 10.2 mW, 8.6 mW, on the devices at the output of the optical fiber for the 365 and 470 nm sources, respectively. These powers gave the following power densities of 4.4 mW/cm² (UV) and 3 mW/cm² (blue) with the C-AFM in air, and 7.6 mW/cm² (UV) and 6 mW/cm² (blue) with the C-AFM in UHV, depending on the exact geometries of the set-up. For the switching in solution (Fig. S1), we used a chromatography UV lamp (Vilbert Lourmat, power density 2.7 mW/cm²), and a large band halogen lamp (Schott KL 2500 LCD, power density 74 mW/cm²) for the irradiation in visible.

XPS results.



Figure S2. XPS spectra of LSMO substrate. (a) survey spectrum, and high resolution spectra of (b) C1s, (c) La3d, (d) Sr3d, (e) Mn2p and (f) O1s contributions. The component of the deconvolution, peak area and chemical assignments are analyzed in Table S1.

Spectrum	Peak	Identification	Energy [eV]	Area [a. u.]	ASF [a. u.]	Area / ASF [a. u.]	0,7 × Ratio La
C1s	b1	C-C	284.7	994			
C1s	b2	C-O-C	285.8	405			
C1s	b3	O-C=O	288.4	215			
La3d 5/2	c1	La (LSMO)	833.9	11466			
La3d 5/2	c2	satellite	835.9	3697			
La3d 5/2	c3	satellite	838.1	10854			
La3d 3/2	c4	Auger, plasmon	847.3	1952			
La3d 3/2	c5	La (LSMO)	850.6	7291			
La3d 3/2	c6	satellite	852.6	4099			
La3d 3/2	c7	satellite	855	6708			
La3d 5/2 + 3/2	(Sum ci) - c4			44115	7.708	5723	0.7
Sr3d 5/2	d1	Sr (LSMO)	132.4	2213			
Sr3d 3/2	d2	Sr (LSMO)	134.1	2036			
Sr3d 5/2 + 3/2	Sum di			4249	1.578	2693	0.33
Mn2p 3/2	e1	Mn3+	641.3	5080			
Mn2p 3/2	e2	Mn4+	643	5556			
Mn2p 1/2	e3	Mn3+	652.8	4505			
Mn2p 1/2	e4	Mn4+	655	1599			
Mn2p 3/2 + 1/2	Sum ei			16740	2.42	6917	0.85
O1s	f1	Mn oxide	529.1	9740			
O1s	f2	La oxide	530.7	5326			
O1s	f3	Sr oxide	532.4	1331			
O1s	Sum fi			16397	0.711	23062	2.82

Table S1. Deconvolution of the XPS peaks and chemical assignment, peak energy, peak area, atomic sensitivity factor (ASF), ASF corrected contribution of each chemical element, and deduced stoichiometry of LSMO assuming a weight 0.7 for La. Peak assignation from Refs. 7, 8.



Figure S3. XPS spectra of LSMO/DDA sample. (a) survey spectrum, and high resolution spectra of (b) C1s, (c) La3d, (d) Sr3d, (e) Mn2p, (f) O1s, (g) P2s and (h)

S2p contributions. The component of the deconvolution, peak area and chemical assignments are analyzed in Table S2.

Spectrum	Peak	Identification	Energy [eV]	Area [a. u.]	ASF [a. u.]	Area / ASF	0,7 × Ratio La	2,0 × Ratio S
C1s	b1'	C-C	284.8	6638				
C1s	b1'-b1	C-C		5644	0.296	19067		31.78
C1s	b2'	C-O-C	285.9	593				
La3d 5/2	c1'	La (LSMO)	834.3	2543				
La3d 5/2	c2'	satellite	836.5	1084				
La3d 5/2	c3'	satellite	838.4	1936				
La3d 3/2	c4'	Auger, plasmon	847.9	255				
La3d 3/2	c5'	La (LSMO)	850.8	1662				
La3d 3/2	c6'	satellite	852.9	1070				
La3d 3/2	c7'	satellite	855.3	1583				
La3d 5/2 + 3/2	(Sum ci') - c4'			9878	7.708	1282	0.7	
Sr3p 3/2	d1'	Sr oxide	286.2	668				
Sr3p 1/2	d2'	Sr oxide	278.4	241				
Sr3p 5/2 + 3/2	Sum di'			909	1.536	592	0.32	
Mn2p 3/2	e1'	Mn3+	641.2	1177				
Mn2p 3/2	e2'	Mn4+	643.1	972				
Mn2p 1/2	e3'	Mn3+	653.2	796				
Mn2p 1/2	e4'	Mn4+	655.6	217				
Mn2p 3/2 + 1/2	Sum ei'			3162	2.42	1307	0.71	
O1s	f1'	Mn oxide	529.1	2081				
O1s	f2'	La oxide, PO(OH)2	531.3	5286				
O1s	f3'	Sr oxide, PO(OH)2	533.2	1171				
O1s	Sum fi'			8538	0.711	12008		
P2s	g1'	PO(OH)2	190.6	388	0.355	1093		1.82
S2p 3/2	h1'	C-S-C	164	564				
S2p 1/2	h2'	C-S-C	165.3	120				
S2p 3/2 + 1/2	Sum hi'			684	0.57	1200		2

Table S2. Deconvolution of the XPS peaks and chemical assignment, peak energy, peak area, atomic sensitivity factor (ASF), ASF corrected contribution of each chemical element, deduced LSMO stoichiometry assuming a weight 0.7 for La, and DDA stoichiometry. Peak assignation from Refs. 7, 8.

Variability of the LSMO substrates.



Figure S4. Sample #1: (**a**,**b**) Topographic AFM images (in air) (1x1 μ m² and 0.5x0.5 μ m², respectively). (**c**) Current (C-AFM) images (log scale) at 2V, 0.5x0.5 μ m². Sample #2: (**d**,**e**) Topographic AFM images (in air) (1.6x1.6 μ m² and 1x1 μ m², respectively). (**f**) Current (C-AFM) images (log scale) at 0.5 V , 1x1 μ m².



Repeatability of the stress effect on the LSMO sample.

Figure S5. (a) C-AFM image (log scale, at 0.5V and loading force 30 nN) for 3 successive zones with increasing areas (1: $0.5 \times 0.5 \ \mu m^2$, 2: $2 \times 2 \ \mu m^2$ and 3: $2 \times 2 \ \mu m^2$ rotated by 45°. (b) Current profile averaged on several image lines inside the white rectangle.

Conductance switching of the LSMO at 0 V bias.



Figure S6. (a) Topographic AFM images and (**b**) C-AFM images (current in log scale) of two zones scanned successively by increasing the scanned area dimensions ($0.5x0.5 \ \mu m^2$ at 0 V and loading force of 30 nN marked by the dashed line, and $1.2x1.2 \ \mu m^2$ at 0.1 V loading force 30 nN). (**c,d**) height and current profile averaged on several image lines inside the white rectangles.











Figure S7. (a) 2D histogram of current-voltage measurements of the LSMO/DDA samples (middle figure) and 1D histograms at -0.3 V and +0.3 V (left and right figures). The number of measurements on different zones are indicated on the figure, as well as the values of log μ . **(b)** Same data after 5 min irradiation at 365

nm. (c) After 14h in the dark (slow relaxation to the open form). (d) After 10 min blue irradiation at 470 nm. (e) After 10 min irradiation at 365 nm. (f) After 15 min blue irradiation at 470 nm. (g,h) Evolution of the log-mean current at -0.3 and 0.3 V, respectively, under the successive stimulations. All C-AFM measurements under a flux of N_2 and loading force of 30 nN.



Figure S8. (a) 2D histogram of current-voltage measurements of the LSMO/DDA samples and **(b)** 1D histograms at 2 V (313 I-V traces). **(c-d)** Same data after 2 h

irradiation in blue 470 nm (112 I-V traces). **(e-f)** After 2 h irradiation in UV at 365 nm (2152 I-V traces). **(g-h)** After 2h blue irradiation at 470 nm (795 I-V traces). **(i)** Evolution of the log-mean current at +2 under the successive stimulations. A ratio of ca. 5 is observed. All C-AFM measurements under a flux of N_2 and loading force of 30 nN. Note that in this peculiar case, due to the high resistivity of the LSMO substrate, we did not measure current below 1 V and only positive bias were applied for this series of measurements.

Due to a low quality of the SAMs for these two samples (ellipsometry thickness ~1nm compared to 1.7-2 nm for samples shown in Fig. 5, main text), the open/ closed ratio are weak (<5) and we do not try to resolve two conductance peaks. It is likely that the worse quality for these two samples is related to the fact that DDA SAMs were grafted on previously used and recycled LSMO substrates (samples sonicated in DI water 5 min, in ethanol VLSI-grade 5 min, dried under N2 stream, followed by UV-ozone cleaning during 30 min and again the DI water/ethanol cleaning) instead of freshly fabricated LSMO substrate for the other samples.

Effect of long time UV irradiations.

Figure S9 shows the 2D current histograms before and after the 365 nm irradiation (6 h) measured by C-AFM (ambient condition). Before irradiation, we

measured a broad current distribution, which can also be decomposed in two peaks: P1 log μ = -11.92 (1.2x10⁻¹² A) , P2 log μ = -9.59 (2.6x10⁻¹⁰ A) at -045 V (and almost the same values at 0.45 V). However, after the 365 nm irradiation, we observed a narrow distribution with only the peak P1 (Figs. S9d-f). Note also that only a small number of I-V traces have been recorded (46 compared to 521), which means that large parts of the sample have a current below the sensitivity of our C-AFM (1 pA). This result is surprising since we expect an increase of the molecular conductance when the diarylethenes are in the closed from.⁹⁻¹² Then, we exposed the sample to a 470 nm during 6h (switching DDA-c to DDA-o) and we remeasured the current (Figs. S9g-i). No change was observed.

Thus, no reversible optical switching of DDA is detected in the LSMO/DDA samples in this case. A possible expansion would be that long times (6h) irradiation at 365 nm can induce the blocked form of the diarylethne¹³ for which we suppose a very low conductance.



Figure S9. (a) 2D histogram of current-voltage measurements of the LSMO/DDA sample (521 I-V traces) and **(b,c)** 1D histograms at -0.45 V and +0.45 V. **(d)** 2D histograms of current-voltage measurements of the DDA SAM after 6 h irradiation at 365 nm (46 I-V traces) and **(e,f)** 1D histograms at at -0.45 V and

+0.45 V. (g) 2D histogram of current-voltage measurements of the LSMO/DDA sample after 6 h irradiation at 365 nm and 6h irradiation at 470 nm (34 I-V traces) and (h,i) 1D histograms at -0.45 V and +0.45 V. All measurement by C-AFM in air and loading force of 30 nN. The black lines are the fits with a log-normal distribution. The fit parameters, log-mean current (log μ) and log-standard deviation (log σ) are given in the figures. Note that the relatively small number of I-V traces in these histograms (while around thousands were acquired, see details in the supporting information) is due to the fact that a majority of the traces showed currents <2x10⁻¹² A, close to the sensitivity and noise level of our apparatus, and were removed for clarity. Nevertheless, a number of counts >20-30 is reasonably sufficient to a significant statistical analysis of C-AFM measurements on SAMs.¹⁴

Effect of long time UV irradiations on a bare LSMO sample.

We irradiated a bare LSMO sample in the same conditions as in Fig. S9 (365 nm, 6h) and measured the I-V curves (Fig. S10). We observed a current decrease by a factor 16 from log $\mu \approx -8.8$ (1.6x10⁻⁹ A) to -10 (10⁻¹⁰ A). This persistent photoresistivity (PPR) effect in LSMO¹⁵ - increase of LSMO resistance (a factor about 15) after a long time UV light irradiation - can also contribute to the total current decrease observed (Fig. S9) for the LSMO/DDA sample. We discard the possibility that a long time UV irradiation had severely degraded (removed) the

SAM, because in that case, we would have observed, in the histograms Figs. S9d-f, a second current peak (with a significant number of counts) centered at around 10⁻¹⁰ A as shown in Fig. S10d-f for the LSMO substrate alone. Albeit UV light can generate ozone, which is well known and frequently used to remove organic compounds on a surface, we note that we have used an "ozone-free" UV source (centered at 365 nm with a bandwidth of 10 nm, no UV light at 185 nm), which minimize the risk of SAM degradation.



Figure S10. (a-c) 2D histogram of current-voltage measurements of the LSMO substrate (800 I-V traces) and 1D histograms at -0.1 V and +0.1 V. (d-f) 2D histogram of current-voltage measurements of the LSMO substrate after 6 h

irradiation at 365 nm (800 I-V traces) and 1D histograms at -0.1 V and +0.1 V. All C-AFM measurements in air and loading force of 30 nN.

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