Supplementary information for:

Investigation of the interactions between organophosphorous agents and TiO_2 modified microcantilevers for molecule detection in air

Urelle Biapo,[a]* Denis Spitzer,[b] Valérie Keller,[a] Philippe Bazin[c] and Thomas Cottineau[a]*

XPS

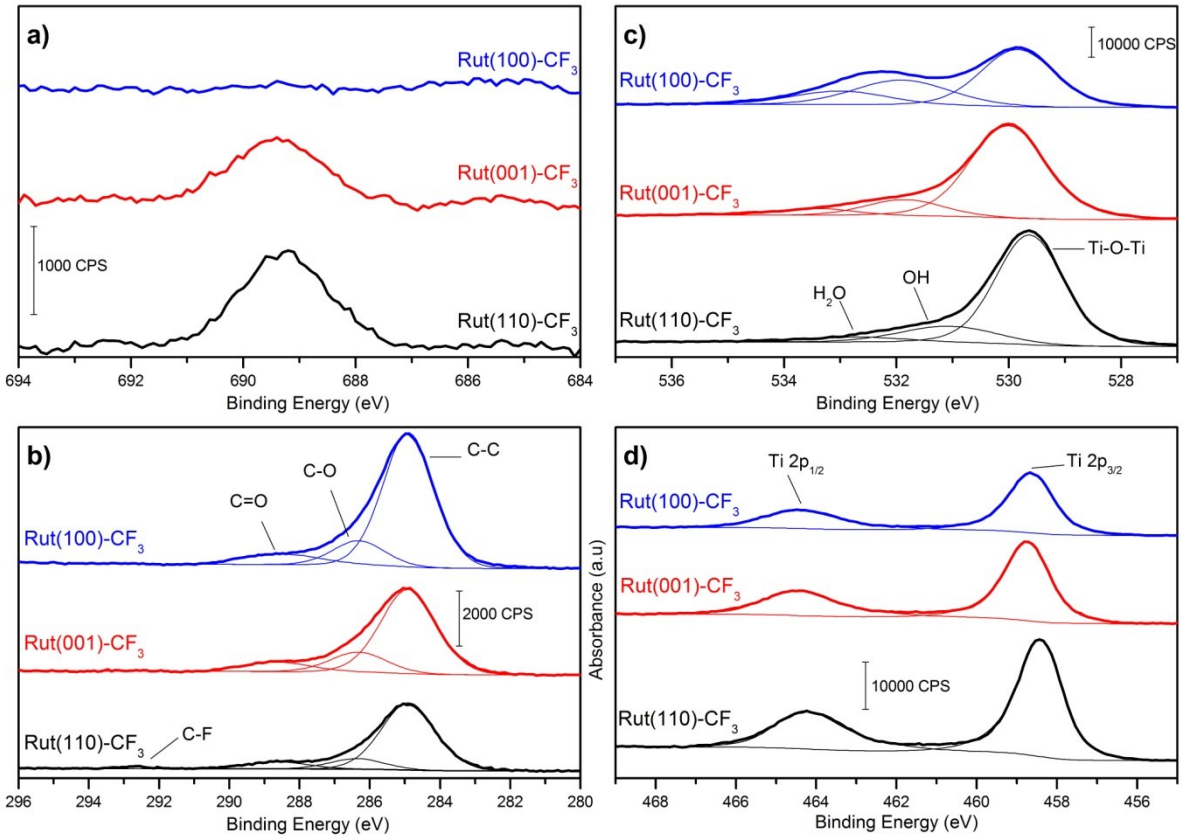

Figure S1: *XPS analysis of (100), (001) and (110) rutile monocristals modified with Fluorine molecules : (a) F 1s (b) C 1s, (c) O 1s and (a) Ti 2p peaks.*

Table S1: *XPS deconvolution parameters for the (100), (001) and (110) rutile monocristals modified with Fluorine molecules.*

		Attribution	Position (eV)	FWHM (eV)	R.S.F.	At conc. %		
Rutile (001) CF_3								
C 1s	A	**C-C**	284.9	1.81	1.00	22.3	**32.0**	
	B	**C**-O	286.2	1.81	1.00	5.9		
	C	**C**=O	288.6	2.50	1.00	3.8		F/Ti
F 1s		C-**F**	688.5	2.01	4.43	1.4	**1.4**	0.11
O 1s	A	Ti-**O**	530.0	1.60	2.93	42.6	**53.0**	
	B	-**O**H	531.9	1.60	2.93	7.3		O_{surf}/O_{bulk}
	C	-H_2**O**	533.4	1.60	2.93	3.1		0.24
Ti $2p_{3/2}$		**Ti**-O	458.7	1.28	5.22	13.6	**13.6**	
Rutile (100) CF_3								
C 1s	A	**C-C**	284.9	1.71	1.00	29.9	**39.3**	
	B	**C**-O	286.3	1.71	1.00	5.6		
	C	**C**=O	288.5	2.71	1.00	3.8		F/Ti
F 1s		C-**F**	688.6	1.67	4.43	0.2	**0.2**	0.02
O 1s	A	Ti-**O**	529.9	1.55	2.93	26.7	**49.5**	
	B	-**O**H	531.9	2.00	2.93	14.8		O_{surf}/O_{bulk}
	C	-H_2**O**	533.0	2.00	2.93	8.0		0.85
Ti $2p_{3/2}$		**Ti**-O	458.6	1.27	5.22	10.7	**10.7**	
Rutile (110) CF_3								
C 1s	A	**C-C**	284.9	1.83	1.00	15.7	**20.0**	
	B	**C**-O	286.4	1.83	1.00	2.3		
	C	**C**=O	288.6	1.98	1.00	1.7		
	D	**C**-F	292.7	0.93	1.00	0.3		F/Ti
F 1s		C-**F**	688.3	1.97	4.43	1.8	**1.8**	0.09
O 1s	A	Ti-**O**	529.7	1.41	2.93	45.6	**57.8**	
	B	-**O**H	531.1	2.00	2.93	9.4		O_{surf}/O_{bulk}
	C	-H_2**O**	532.7	2.00	2.93	2.9		0.27
Ti $2p_{3/2}$		**Ti**-O	458.4	1.27	5.22	20.4	**20.4**	

DMMP detection curves

The µcantilever frequency shift associated to DMMP adsorbtion and desorption du DMMP were fitted by a biexponential decay fonctions.

$$\Delta f_{ads} = \Delta f_0 + A_1 e^{-\frac{x - x_0}{t_1}} + A_2 e^{-\frac{x - x_0}{t_2}}$$

Single exponential function cannot reproduce correctly the curves. This suggests that two different phenomena govern the absorption kinetics. (A_1, t_1) and (A_2, t_2) are the constant associated to these phenomena and our hypothesis is that the fast transition is associated with physical adsorption/desorption at the film surface while the slower one is related to chemical interaction with the surface and diffusion in the porosity of the TiO_2-NRs films. All fitting were done with Origin program. Figure S2 gives an example of data fitting for the pristine TiO_2 nanorods. The constants ectracted for the different samples are gathered in table S2.

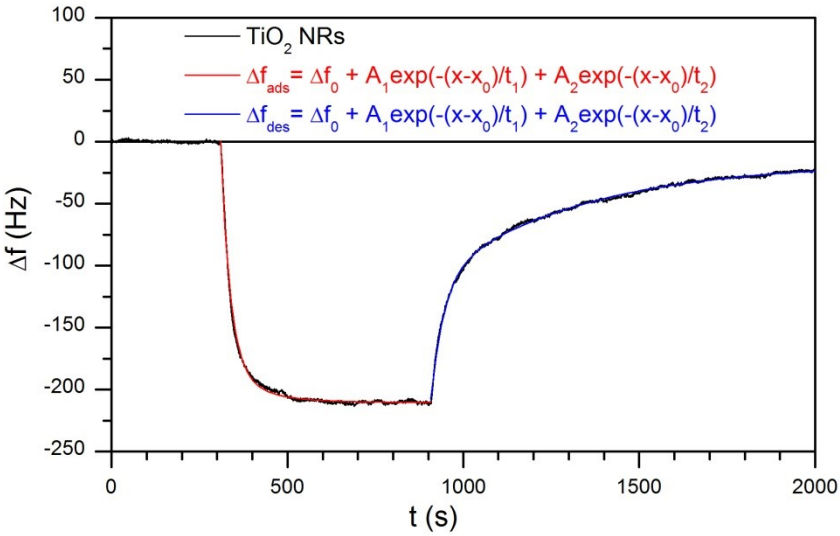

Figure S2: *Example of fitting of the frequencies shift curves during the DMMP absorption / desorption on the microcantilever.*

Table S2: *Fit parameters of the frequency shifts during DMMP absorption/desorption for the µcantilevers modified with different molecules.*

		Adsorption					*Desorption*	
	Δ_{f10min} (Hz)	A_1 (Hz)	t_1 (s)	A_2 (Hz)	t_2 (s)	A_1+A_2 (Hz)	t_1 (s)	t_2 (s)
TiO_2	-210.0	183.0	27.3	27.8	**103.1**	210.8	37.2	**419.0**
Fluorine	-312.0	216.0	26.4	98.0	**30.8**	314.0	25.7	**118.9**
Oxime	-372.0	238.3	19.6	151.8	**235.5**	390.1	32.6	**352.7**
Amine	-604.0	260.6	36.8	386.8	**238.3**	647.4	73.9	**499.8**

In situ TDP followed by IR measurements.

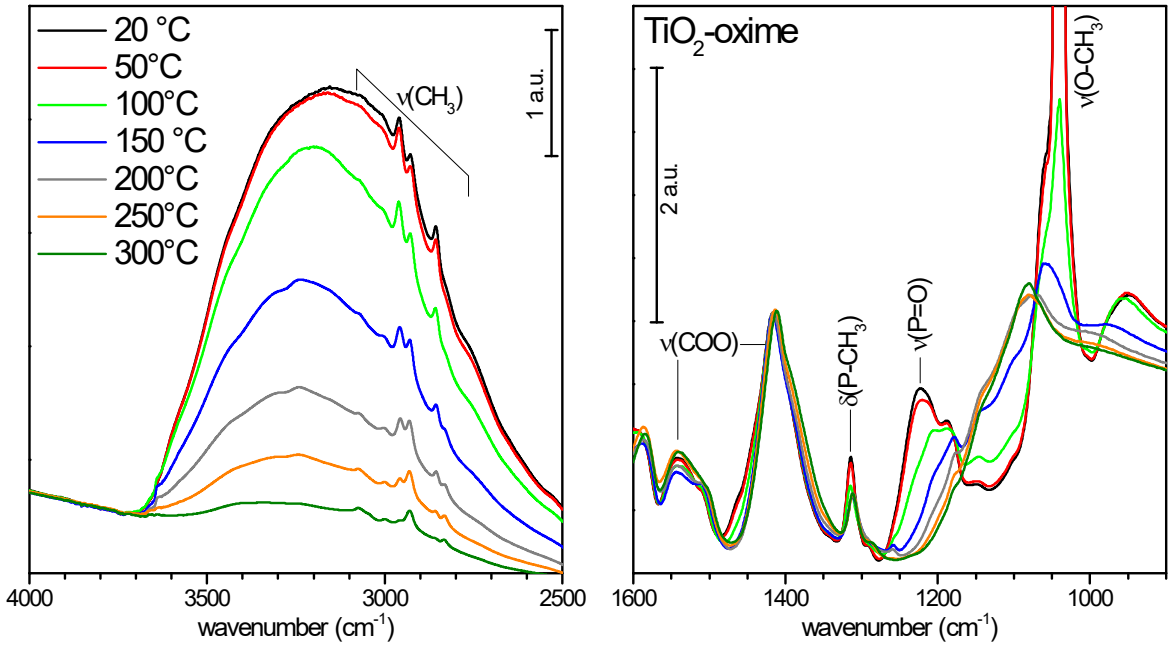

Figure S3: *IR patterns of TiO_2–oxime recorded during the thermal programmed desorption between 20 and 300°C.*

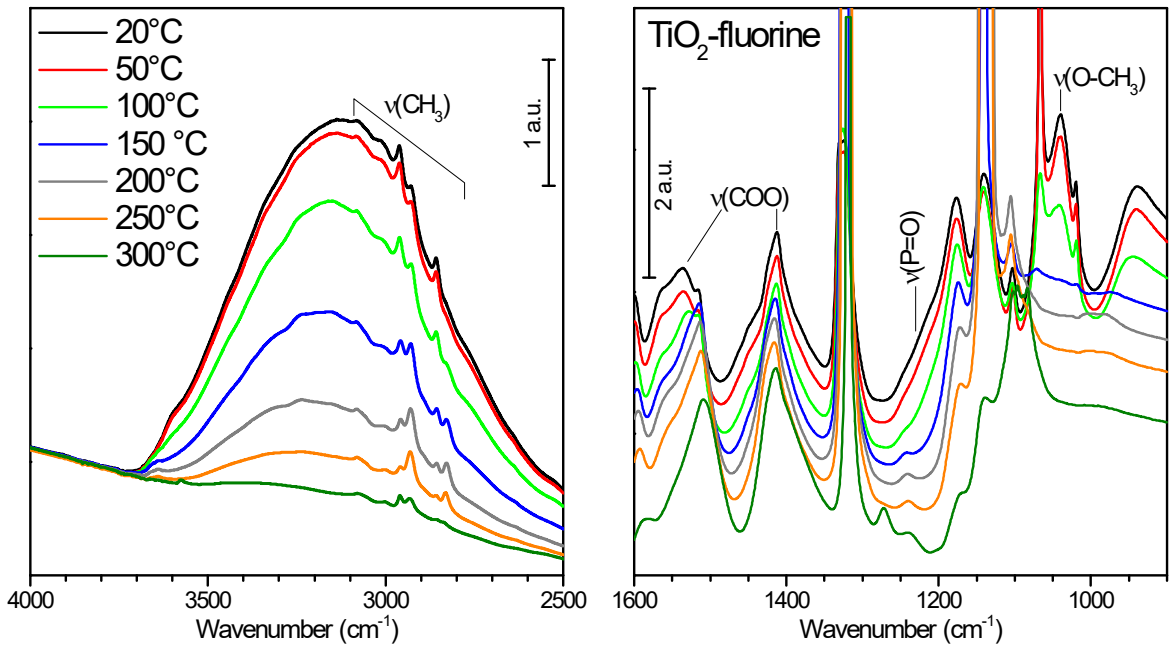

Figure S4: *IR patterns of TiO_2–fluorine recorded during the thermal programmed desorption between 20 and 300°C.*

Role of water and interfering molecules

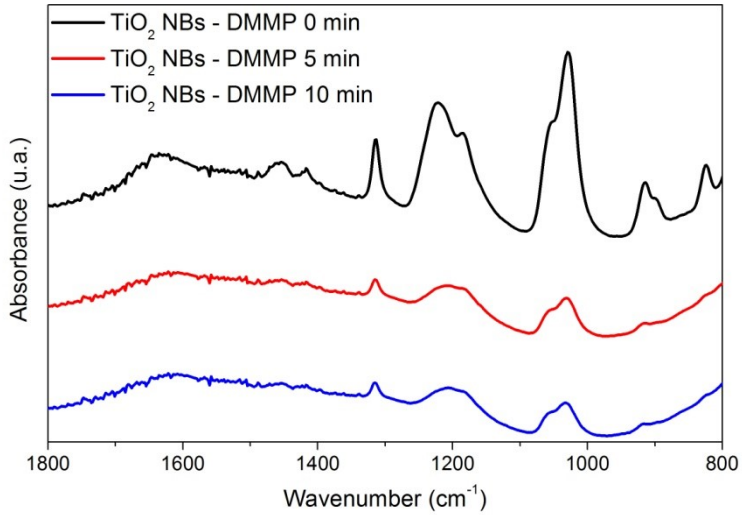

Figure S5: *Evolution of IR signal measured by ATR on a SI surface nanostructured with TiO_2 NRs exposed in ambient air after exposition of concentrated DMMP vapour. At t=0 min, the sample is removed from the DMMP atmosphere IR spectra are recorded after 0, 5 and 10 min of air exposition.*

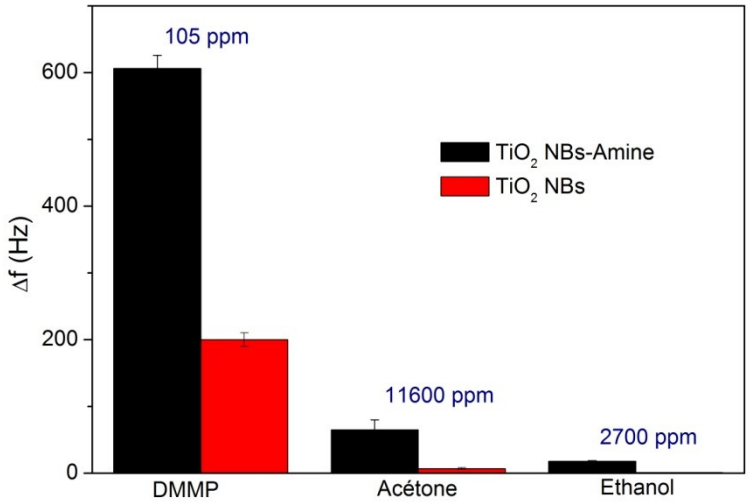

Figure S6: *Response of a nanostructured µcantilever and a µcantilever nanostructured and functionnalized with amino terminated molecules when exposed to 50 mL.min^{-1} flow of air with DMMP, acetone or ethanol. Note that the concentrations of ethanol and acetone in air are order of magnitude higher than the one of DMMP.*