Supplementary Information for:

# Intermediate Band in the Gap of Photosensitive Hybrid Gel Based on Titanium Oxide, Role of Coordinated Ligands During Photoreduction.

Thomas Cottineau, Annabelle Rouet, Vincent Fernandez, Luc Brohan and Mireille Richard-Plouet\*

> Institut des Matériaux Jean Rouxel (IMN) Université de Nantes/CNRS 2 rue de la Houssinière 44322 Nantes, (France)

#### 1. Solid state <sup>1</sup>H NMR

In the high vacuum condition of the XPS experiment a part of the organic components of the TiDMF gel is expected to desorbing from the sample. In order to have an indication on which organic species remain by strong interacting with the inorganic part and which will desorb, solid state NMR experiments were conducted on the TiDMF gel. As already proven by liquid <sup>1</sup>H NMR, the different species involved in the TiDMF sol could be isolated and identified, but this analysis was not possible for the TiDMF gel or aged sol due to their high viscosity.

For solid state NMR experiments, the fresh sol was introduced in the sample holder and then heated at 70 °C for 24 h prior being placed in the rotor. <sup>1</sup>H single pulse spectra were acquired at room temperature on a Bruker Advance spectrometer operating at 500.13 MHz using a Bruker Magic Angle Spinning, (MAS) probe with tetramethylsilane (TMS) as external reference. A 14 kHz MAS spinning rate, a  $\pi/2$  pulsewidth of 4 µs and a recycle time of 1 s were used for these measurements.

A typical solid state <sup>1</sup>H NMR spectrum of TiDMF gel is presented in **figure S1**. A large peak associated to -NH<sub>2</sub> of DMACl is located at 8.47 ppm. Methanoic acid appears as two components, one large (*l*.) at 8.38 ppm and a narrow (*n*.) one at 8.36 ppm. Similarly, two contributions located at 8.09 (*l*.) and 8.08 (*n*.) ppm appears for the aldhehyde-like proton of DMF. Protons of water molecule, hydroxonium cation and/or acid proton of methanoic acid are detected as two peaks, at 5.76 (*l*.) and 5.70 (*n*.) ppm. In the range of protons belonging to methyl groups, N,N-dimethylformamide gives four contributions fitted as two doublets: (i) 2.86 (*n*.)/2.87 (*l*.) ppm and 3.04 (*n*.)/3.06 (*l*.) ppm. The last peak decomposed as two components at 2.78 (*n*.) and 2.80 (*l*.) ppm is attributed to methyl group of DMACl.



*Figure S1*: solid state <sup>1</sup>H NMR spectra for a TiDMF gel heated at 70°C for 24 h (up), zoom of the different regions of interest and fit using Lorentzian functions (down).

For quantification, the DMACl over Ti ratio (after heating) is fixed to 3.4. We checked that the area of aldehyde-like proton over the area of protons belonging to methyl group is close to 1/6 for DMF with a measured value of 1/5.7. Quantification between the organic species leads to the following formulation:  $(TiO_2, zH_2O)_{polymer} + 3.4 DMACl + 1.8 HCOOH + 1.8 DMF$ . The comparison of these values to the expected formulation proves that volatile species, such as methanoic acid, could partly be released out of the gel (here 47%) during heating in the rotor. Despite DMF is not particularly volatile ( $T_b=153^{\circ}C$ ), it seems that 40% DMF is also expelled from the gel.

The presence of two components for the different species (except  $-NH_2$ ), a narrow and a broad one, indicates that a part of the organic molecules is more mobile that the other one. As the sample is composed of inorganic Ti-O based layers in interaction with a liquid (composed of DMF, HCOOH, DMACl and H<sub>2</sub>O), we infer that the larger contribution is due to molecules in close interaction with the solid part of the gel. From the proportion between these two contributions, the following formulation can be proposed for the solid part of the gel: (TiO<sub>2</sub>, zH<sub>2</sub>O)<sub>polymer</sub> + 0.8 DMACl + 1.3 HCOOH + 1.4 DMF.

## 2. Evolution of XPS contributions under UV in situ illumination.



*Figure S2*: *a) Modified XPS sample holder for in situ UV irradiation. b) Sample holder in irradiation position and c) in measurement position.* 



In **figure S2**, is presented the modified XPS sample holder for *in situ* UV irradiation of the TiDMF gel.

In **figure S3.a** is presented the evolution of the atomic composition of the solid part of the TiDMF gel depending on the UV illumination time.

In the bottom part of the figure the complete evolution of the different components of C 1s (fig. S3.b), O1s (fig. S3.c) and N 1s (fig. S3.d) is presented

**Figure S3:** Evolution of a) the atomic composition the TiDMF gel under UV irradiation and detailed XPS component evolution (normalized to Ti atoms) under UV illumination for b) carbon  $(C_p(\circ), C_a(\Box), C_b(\Delta))$ , c) oxygen  $(O_a(\circ), O_b(\Box), O_c(\Delta) \text{ and } d)$  nitrogen  $(N_a(\circ), N_b(\Box))$ .

#### 3. Angular XPS experiments

The fast initial evolution of the different components measured by XPS suggests that crystallized DMACl is quickly degraded under X-ray and/or UV illumination. This degradation induces a pressure increase in the analyzing chamber (one order of magnitude while illuminating for 2 h), that can be related to desorption of dimethylamine and HCl as by-products of DMACl photodegradation. The value of DMA formed and Cl 2p in excess suggest that dimethylamine or its degradation products is more efficiently remove from the TiDMF than the associated chloride counterpart.

To clarify the location of DMACl and its degradation, angular dependence XPS analysis of the C<sub>a</sub> 1s, N 1s and Cl 2p peaks was conducted. As observed in **figure S4**, before UV illumination, the quantity of DMACl components is increasing for  $\Box$   $\theta$  ranging from 0 to 60°. It indicates that DMACl is not homogenously distributed in the thickness of the TiDMF gel when the sample is introduced in the XPS chamber. At the end of the angular measurement experiment, DMACl components spectra are recorded with the angle back at  $\theta=0^{\circ}$  and a decrease of these components is observed (in comparison with the initial  $\theta=0^{\circ}$  measurement), indicating its degradation under X-ray irradiation. After 18 hours of UV illumination, the same experiment shows a reduced angular dependence of these components. These results prove that DMACl preferentially crystallizes at the surface of the gel under vacuum and the fast initial evolution is thus related to its degradation.



**Figure S4:** Angular dependence of  $N_b(\circ)$ ,  $N_a(\Box)$ ,  $C_a(\Delta)$  and  $Cl(\diamondsuit)$  percentages before illumination (open symbols), and after UV illumination for 18h (solid symbols).

## 4. UV visible spectra treatment

A typical Tauc plot (with n = 0.5) for the TiDMF gel irradiated under UV light is presented in **figure S5.a**. We infer that the broad band centered on 1.5 eV is due to the transition between the intermediate and conduction bands and the absorption edge between 2.5 and 3 eV is due to the transition between the valence and intermediate band. In order to measure the energy associated to the different transition the measured signal was treated according to the following procedure (**figure S5** is an example of the different steps of the analysis on the sample illuminated under UV for 24h):

First the contribution of the transition between VB and CB is removed by subtracting the spectra of the non illuminated TiDMF gel. The result is presented in **figure S5.b**. Then the strong absorption band in the visible range is fitted with Gaussian curves (**figure S5.c**). The two peaks at 1.2 and 1.8 eV are removed and finally the Tauc plot corresponding to the transition VB to IB is obtained (**figure S5.d**) and the linear domain can be fitted. The linear domain are fitted by looking for the maximum of the first derivate of the data to find the inflexion point and the slope of the linear domain. The results of these fits for the transition between the CB and IB and between IB and VB are presented in **figure S6**.



*Figure S5:* Treatment of the UV-vis absorption spectra for TiDMF gel illuminated with UV for 24h. a) Raw data (a.hv)<sup>0.5</sup>; b) After removal of the spectra of TiDMF gel non irradiated; c) Fit of the absorption in the visible domain; d) After removal of this contribution and fit of the obtain gap.



Figure S6: a) Results of the fit obtained for the VB to IB transition and b) for IB to CB transition.