Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Information

TiO_2 nanoparticles coated with bio-inspired ligands for the Safer-by-Design development of photocatalytic paints

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TEXT S1: Coating rate estimation according to the adsorption mode and denticity of the bio-inspired ligands.

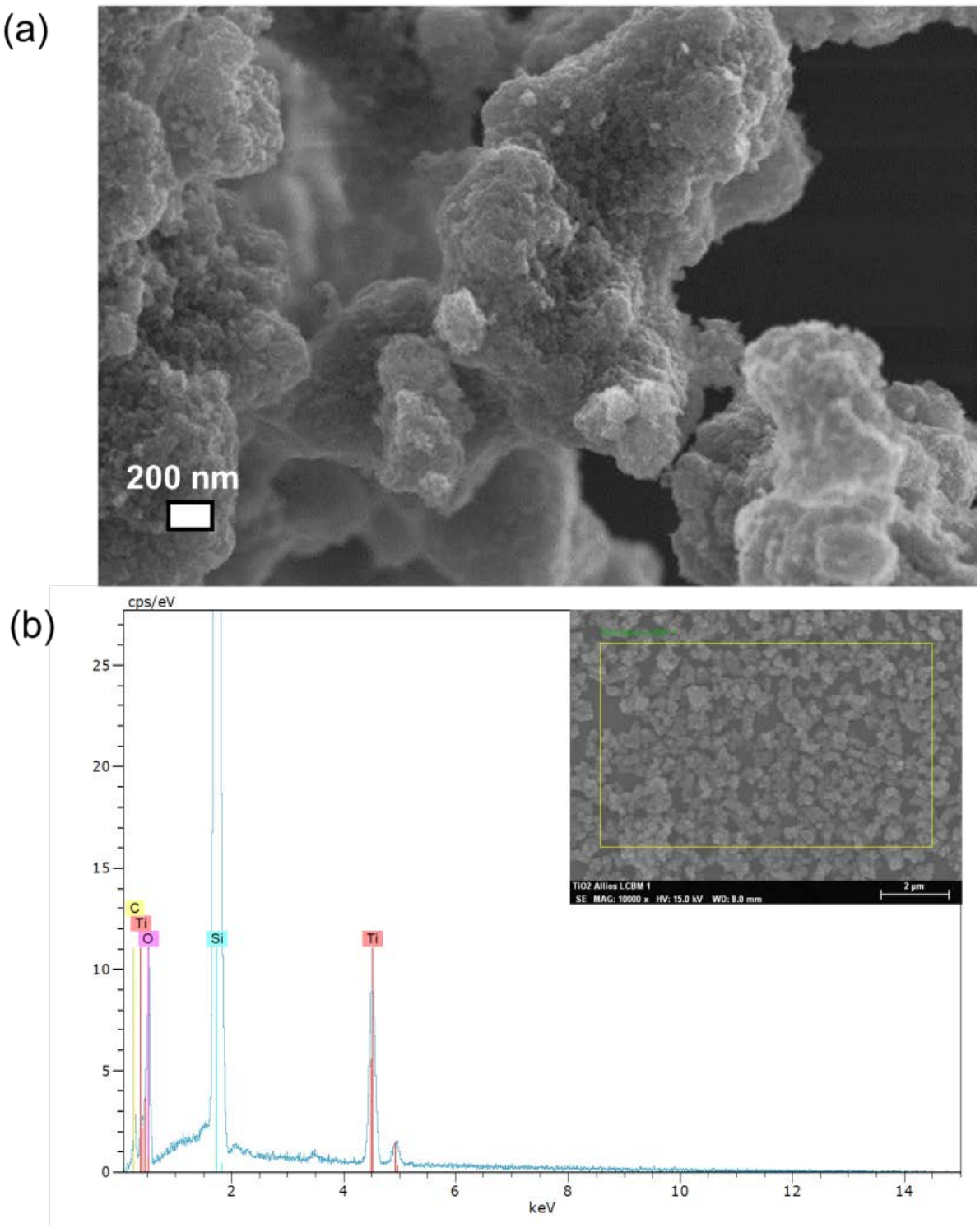

Fig. S1: (a) SEM image and (b) EDX spectroscopy of the TiO_2 NPs.

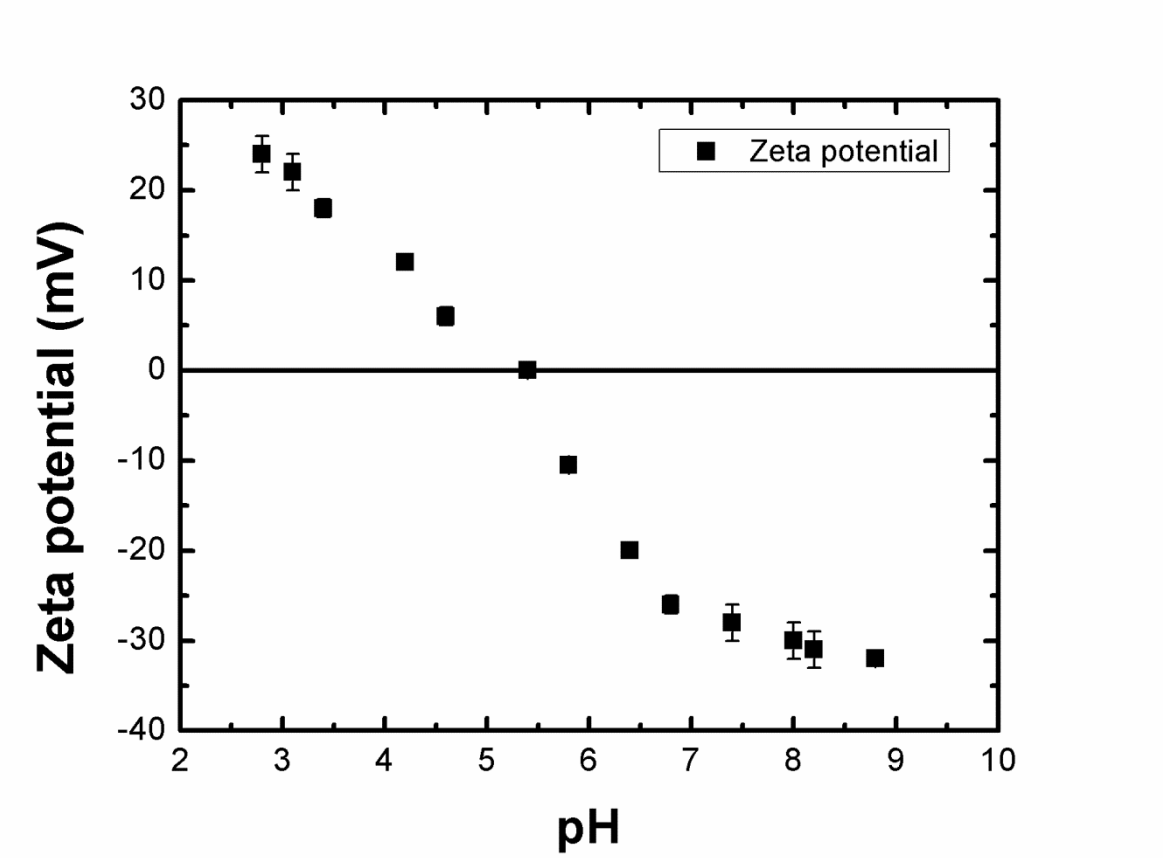

Fig. S2: Zeta potential as a function of pH of a suspension of TiO_2 NPs in DI water (50 $\mu g.mL^{-1}$). The TiO_2 NPs were sonicated for 5 min in 13 mL of deionized water and 10 mM of sodium nitrate ($NaNO_3$). Electrophoretic mobility was measured from low to high pH by adding small amount of nitric acid to adjust the pH.

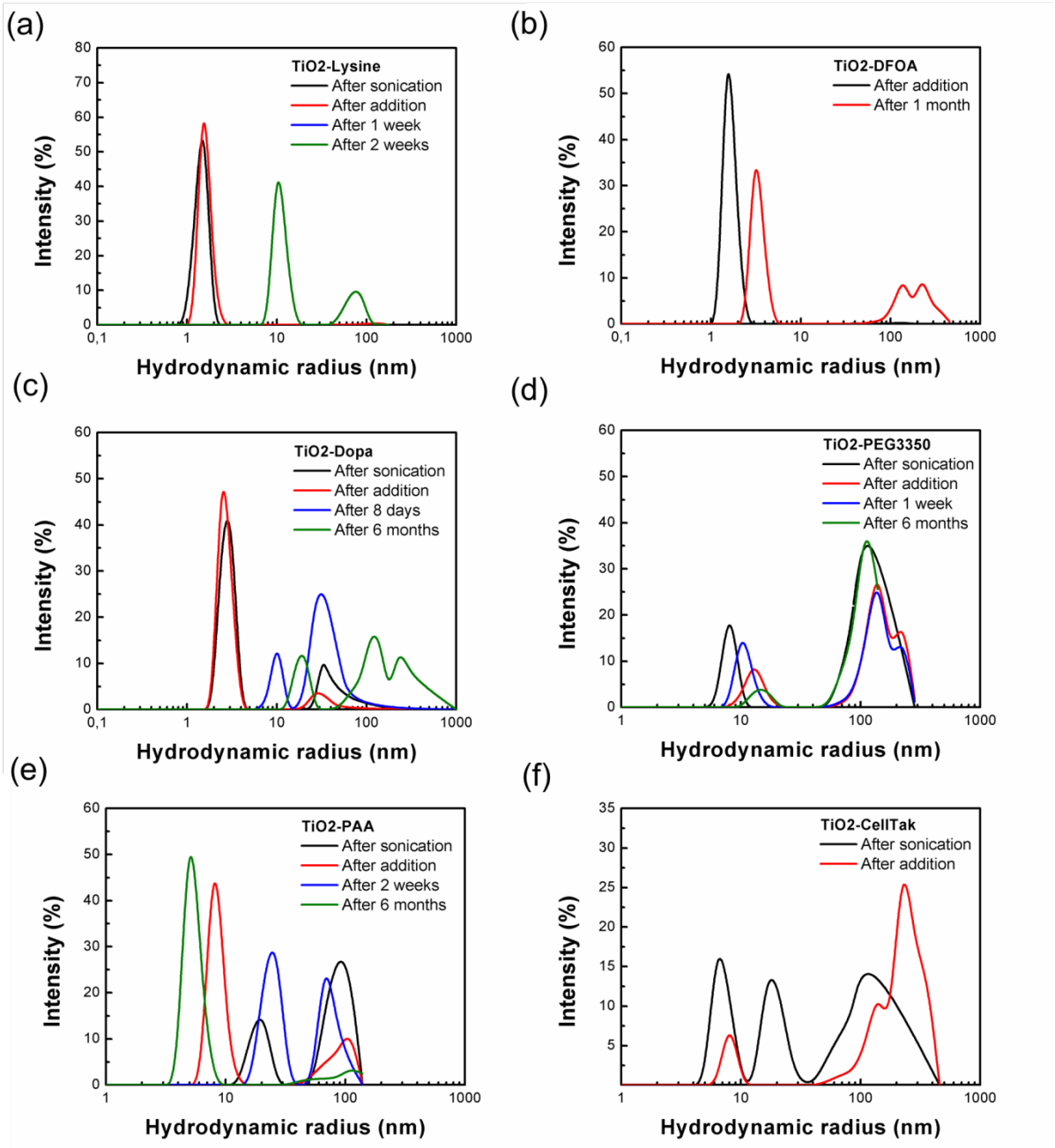

Fig. S3: DLS measurement over time of the TiO_2 NPs size in %Intensity after sonication in presence of pyrophosphate then addition of (a) Lysine, (b) Deferoxamine (DFOA), (c) Dopa (catecholate) (d) PEG3350, (e) PAA and (f) CellTak®.

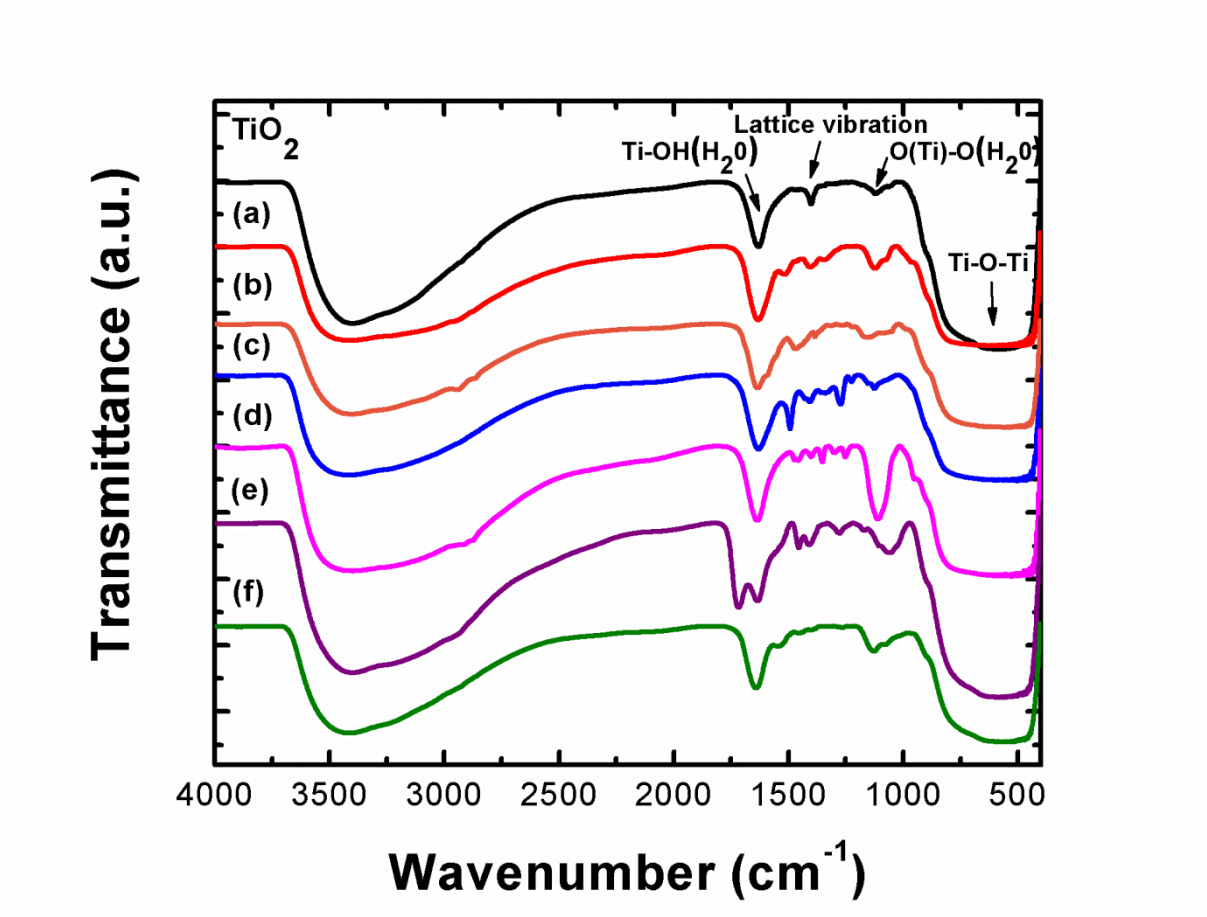

Fig. S4: Full range FTIR spectra in transmittance of the TiO_2 NPs and TiO_2 nanocomposites. In black: TiO_2 NPs and TiO_2 nanocomposites coated with (a) Lysine, (b) Deferoxamine (DFOA), (c) Dopa (catecholate), (d) PEG3350, (e) PAA and (f) CellTak®. The nanocomposites powders were mixed with KBr.

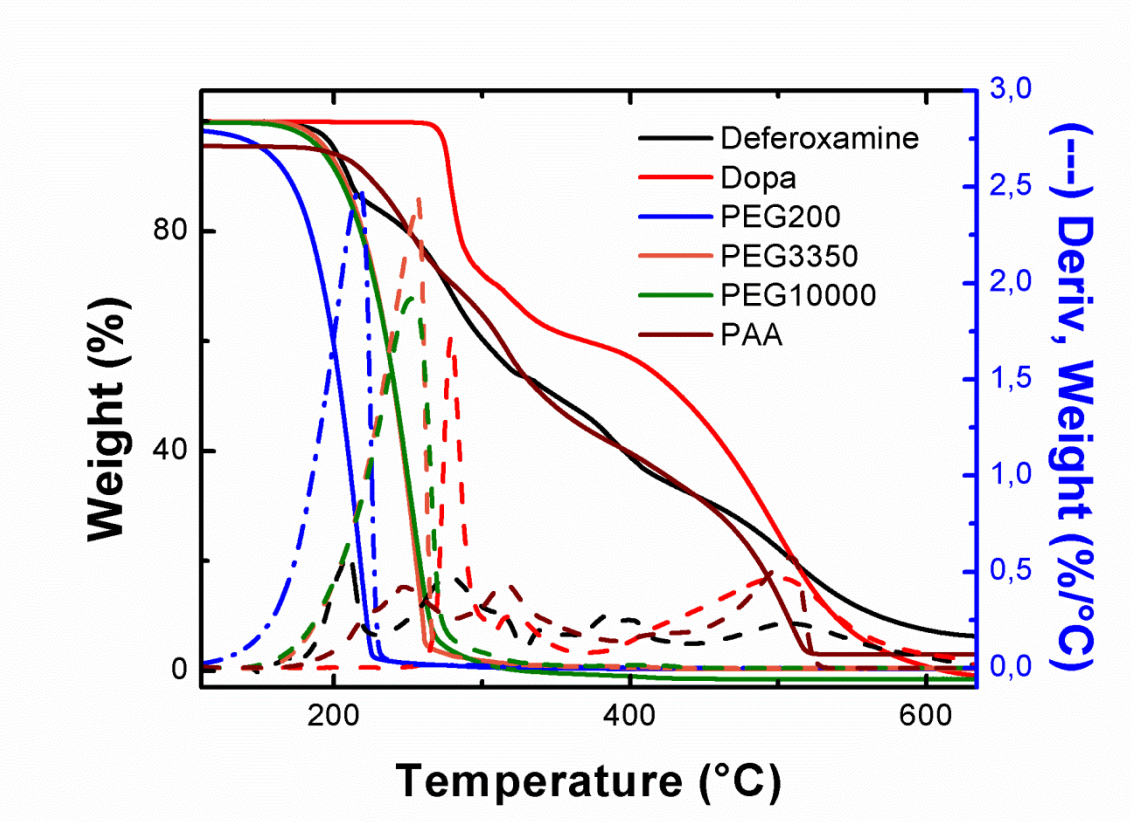

Fig. S5: Thermograms of the free bio-inspired ligands.

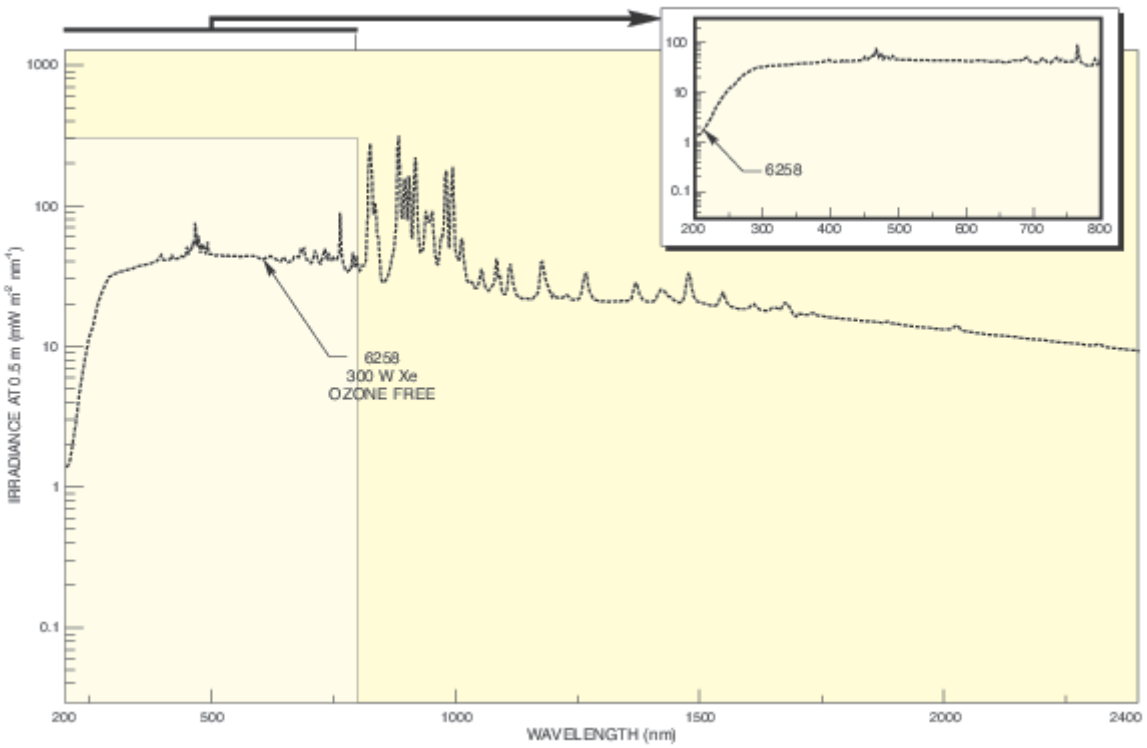

Fig. S6: Emission spectra of the Xenon lamp (300W).

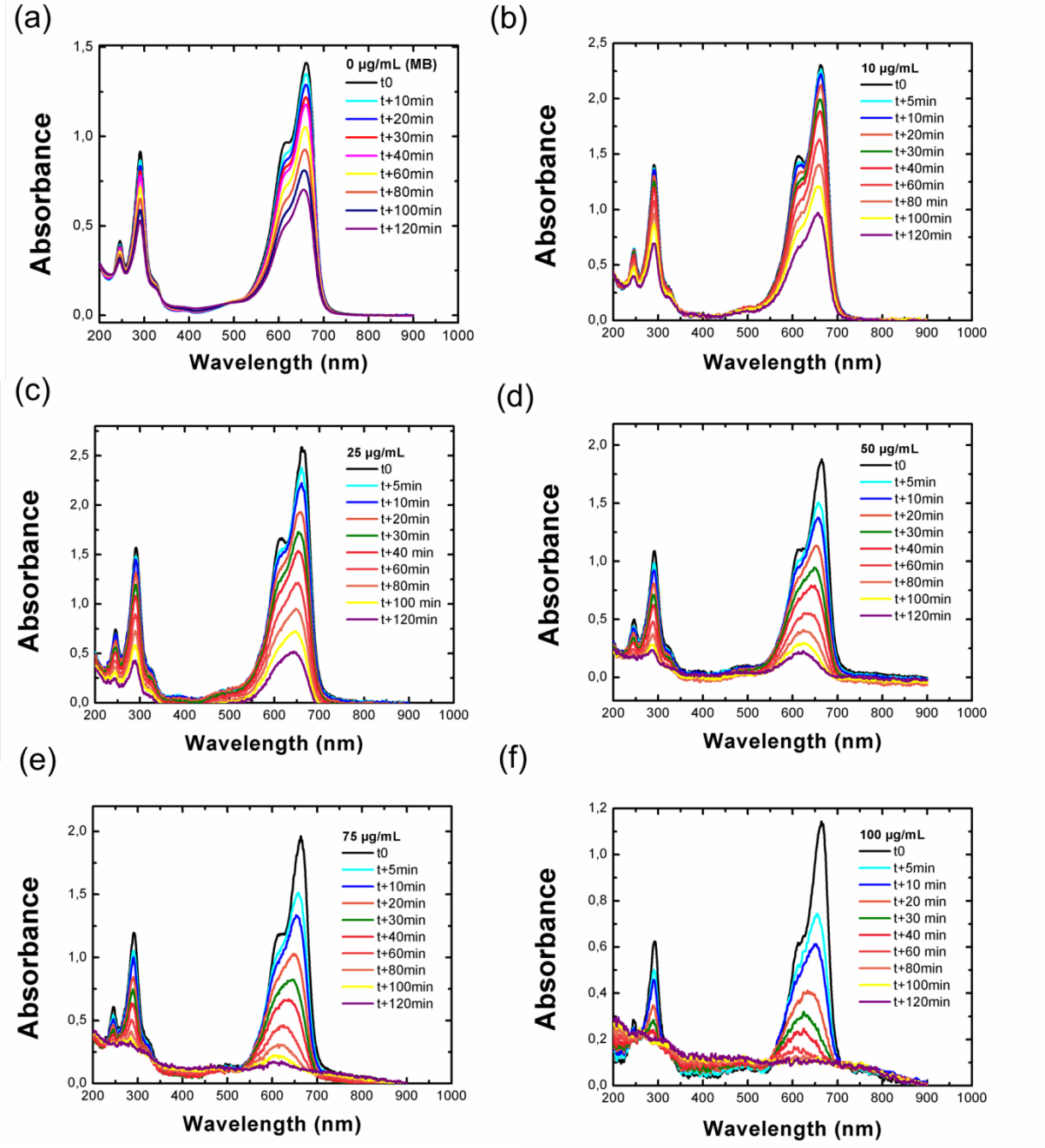

Fig. S7: UV-vis spectroscopy following the degradation under irradiation of MB at a concentration of 12.5 µg.mL^{-1} under UV-vis irradiation by TiO_2 NPs as a function of TiO_2 NPs concentration: (a) 0 µg.mL^{-1}, (b) 10 µg.mL^{-1}, (c) 25 µg.mL^{-1}, (d) 50 µg.mL^{-1}, (e) 75 µg.mL^{-1} (f) 100 µg.mL^{-1}.

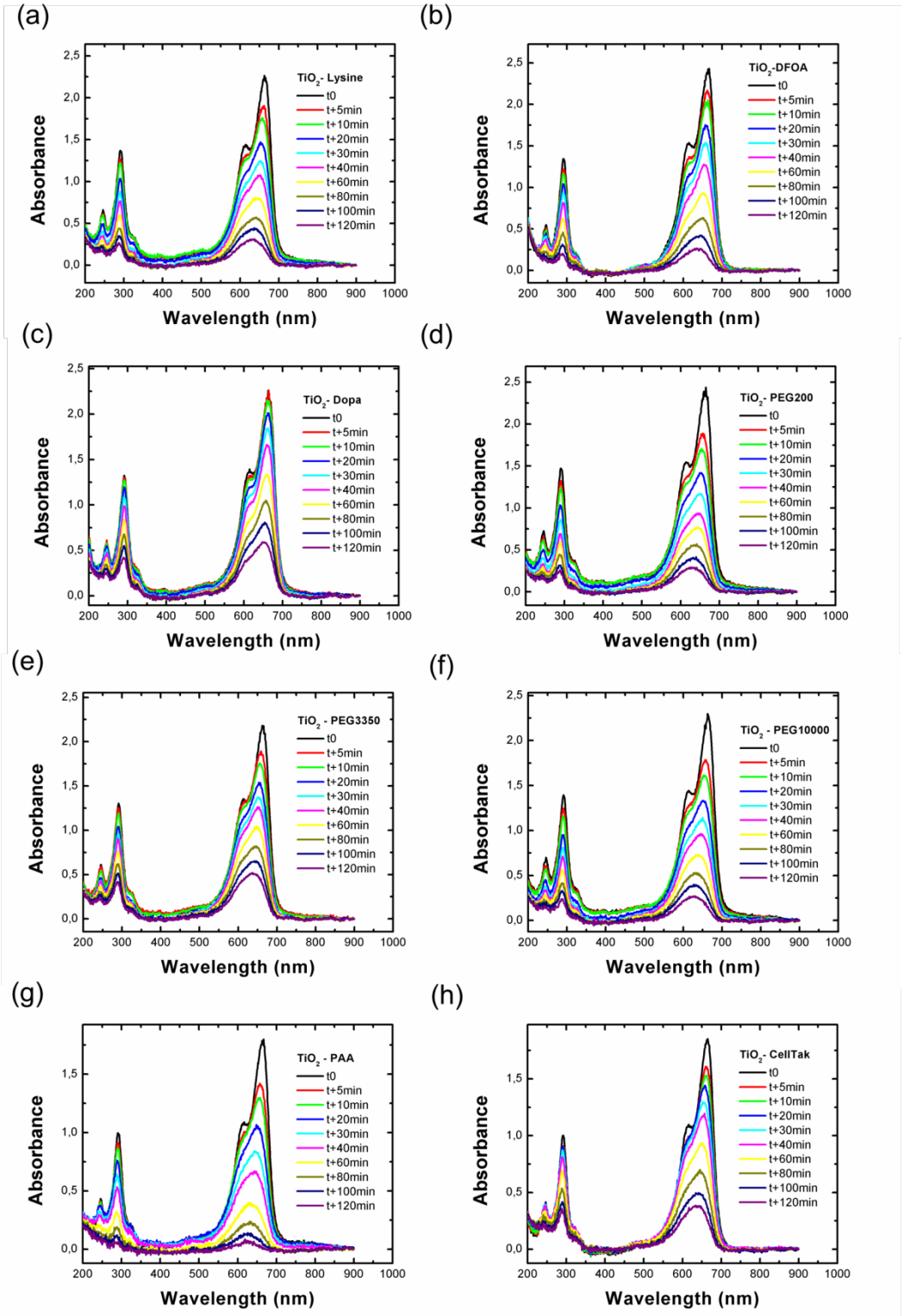

Fig. S8: UV-vis spectroscopy following the degradation of MB at a concentration of 12.5 $\mu g.mL^{-1}$ under irradiation with TiO_2 NPs (50 $\mu g.mL^{-1}$) coated with (a) Lysine, (b) Deferoxamine (DFOA), (c) Dopamine (Dopa), (d) PEG200, (e) PEG3350, (f) PEG10000, (g) PAA and (h) CellTak®.

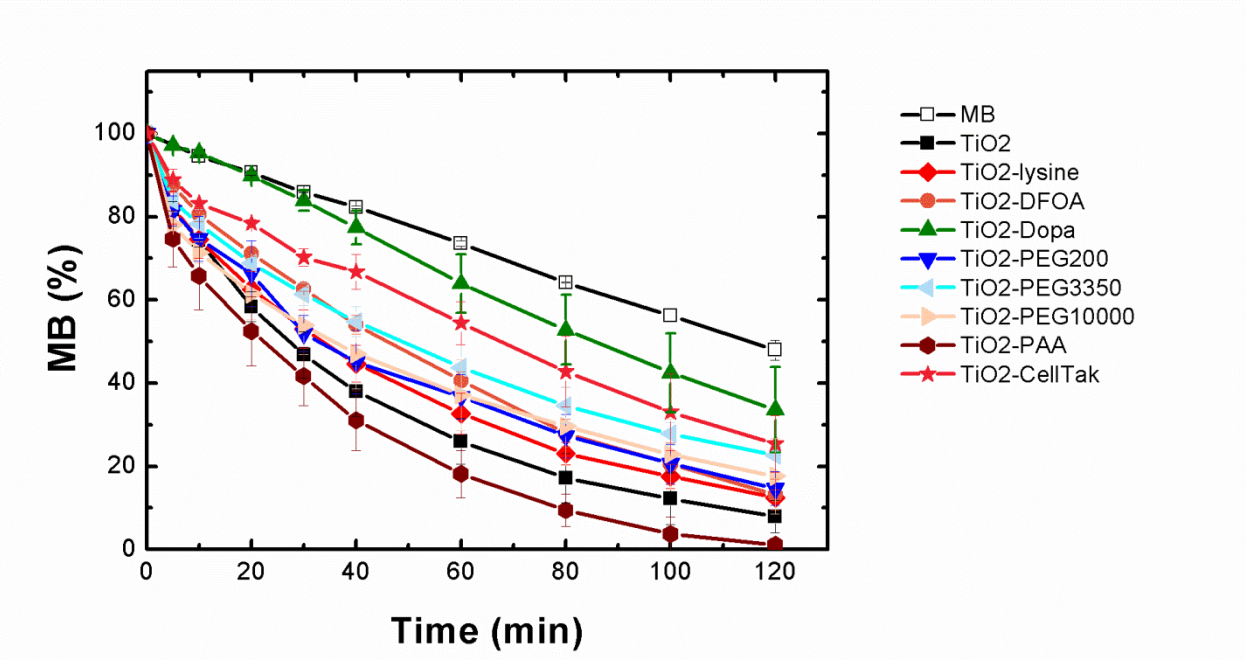

Fig. S9: Degradation of MB at a concentration of 12.5 µg.mL^{-1} under UV-vis irradiation in presence of the different TiO_2 nanocomposites (50 µg.mL^{-1}).

		Electrostatic stabilization conditions (step 1)			Steric stabilization conditions (step 2)					
	Ligand	Electrolyte	$[TiO_2]$ $(mg.mL^{-1})$	Volume dispersion mL	$[Ti]_{Surf}$ (mM)	C_L (mM)	V_L (mL)	Ti_{surf}/Ligand Molar Ratio	pH of the solution of ligand	Color of the collected powder
Bio-molecules	Lysine	H_2pyro	10	8	39	39	8	1/1	11	Beige
	Desferroxamine	H_2pyro	10	8	39	39	8	1/1	8-9	Yellow
	DOPA (catecholate)	NaPyro	10	8	39	$26.1^{(\varphi)}$	12	1/1	8.5	Dark Brown
Bio-polymers	PEG10000	H_2Pyro	10	8	39	39	8	1/1	8	White
	PEG3350	H_2Pyro	10	8	39	39	8	1/1	11-12	White
	PEG200	H_2Pyro	10	8	39	39	8	1/1	11-12	White
	PAA	Napyro	10	8	39	39	8	1/1	2	White
	CellTak®	Pyro neutral buffer* (pH 7)	10	8	39	3.56 µM	4	1/1	> 7	Brown

Table S1: Optimized experimental conditions for the synthesis of the nanocomposites. (*) Pyro neutral buffer: mix 1/1 (volume) of H_2Pyro/NaPyro. The pH of the solutions was adjusted with NaOH or HNO_3 0.1M if necessary, $^{(\varphi)}$ maximum of solubility for Dopa.

(a)

v (cm^{-1})	**TiO_2 attribution**
3700 - 2600	H-bonded stretching vibration at the surface
1620	Coordinated H_2O + Ti-OH
1400	Lattice vibration of TiO_2
1012	O – O stretching vibration
664	Stretching Ti - O - Ti

(b)

v (cm^{-1})	**Bio-coatings attribution**
2900 - 2800	-CH, $-CH_2$
1800 - 1500	Stretching and bending vibration of C=O
1450 - 1350	stretching and bending vibration of C-C
1300 - 1370	Stretching vibration of $C-NH_2$
1100 - 1000	C-O (COOH), O-O stretching vibration

Table S2: (a) Vibration band assignment observed for the TiO_2 NPs contribution and (b) bands attributed to the bio-inspired coating in the different nanocomposite FTIR spectra.

Sample	C1s (%.at)	Ti2p (%.at)	O1s (%.at)
TiO_2	8.30	25.0	63.2
TiO_2-Dopa	21.1	18.7	55.8
TiO_2-PEG3350	20.9	16.8	54.3
TiO_2-PAA	21.4	18.5	58.1
TiO_2-DFOA	22.5	17.5	53.4

Table S3: Chemical composition of the TiO_2 nanocomposites analyzed by XPS.

TEXT S1: Coating rate estimation according to the adsorption mode and denticity of the bio-inspired ligands.

1) Concentration of Ti and Oxygen sites on the surface

From the TiO_2 content found in the powders by TGA, we determined the concentration of Ti sites on the surface (Ti_{surf}) for each nanocomposites. Ti_{surf} for an anatase TiO_2 NPs is given by extracted from [1]:

$$[Ti]_{surf} = [TiO_2] .12.5 / D$$

Where $[Ti]_{surf}$ represents the molar concentration of Ti sites on the surface, $[TiO_2]$ the molar concentration of TiO_2 , and D, the particle diameter expressed in Angstrom (diameter of 4 nm).

Concerning the oxygen sites on surface (O_{surf}), we assumed that two oxygen sites are found per one titanium sites from the representation of an anatase lattice of TiO_2 according to the plane (001). The concentration of surface oxygen available sites is then given by:

$$[O]_{Surf} = 2\ [Ti]_{Surf}$$

2) Ligand adsorption sites

The adsorption mode of the ligand either on the titanium or oxygen surface sites (Ti_{surf} or O_{surf}) was determined according to the XPS analysis. For covalent interaction (Lysine, DFOA, Dopa, CellTak®), the adsorption reaction takes place on the titanium sites while in the case of non-covalent coating involving polymers, surface adsorption would occur by chemisorption via multiple interactions (hydrogen bonds, Van Der Waals contacts) preferentially on the oxygen sites. For PAA, the carboxylate group can have an affinity with the Ti sites, the

[1] Jankovic et al., Nanoscale Res Lett, 2010 ; Chen L. et al., J. Phys Chem B, 1997

calculation was also done by taking into account the two situations (O sites only, Ti and O sites).

3) Denticity

Polymers and the CellTak® poly-dopamine can bind multiple O and/or Ti sites. The denticity (n) of the ligands were calculated by taking into account the number of functional groups in the monomer that can be involved in a bound with the active sites.

This number was estimated according to the formula:

$$n = (M_{polymer} / M_{monomer}).\ p$$

Where $M_{polymer}$ is the molar weight of the polymer, $M_{monomer}$ the molar weight of the monomer and p, the number of functional groups in the polymer that can interact with the surface.

In the particular case of CellTak® that consists in repetition of the decapeptide (Ala-Lys-Pro-Ser-Tyr-Hyp-Hyp-Thr-Dopa-Lys)$_{100}$, we assumed that each peptide can bind one titanium site on the surface. The number of active sites *n* that can be bound with one molecule of CellTak® is then equal to 100 x 10 = 1000. For PEG and PAA, the interactions come from respectively the oxygen atoms (1 per monomer) or the carboxylate group (1 per monomer).

4) Coating rate

Knowing the Ti_{surf} and O_{surf} concentrations in the composites, the adsorption mode of the ligand and their denticity, we deduce the theoretical mass of ligand ($m_{Ligand,\ theory}$) needed to cover all the sites. This is given by the formula:

$$m_{Ligand,\ theory} = [([Ti]_{Surf} + [O]_{Surf}).\ V.\ M_{ligand}] / n$$

where Ti_{surf} and O_{surf} are the concentrations of Ti or O sites involved in the interaction with the ligand (0 if not involved), V is the volume of the suspension in which the particles were dispersed before addition of ligand (8 mL), M the molecular weight of the ligand and n, the denticity of the ligand.

The coating rate (CR) is finally calculated by dividing the experimental mass of the ligand ($m_{Ligand,\ exp}$) found by TGA (weight loss associated with the departure of the ligand) over the theoretical mass of ligand necessary to cover the surface:

$$\text{Coating (\%)} = (m_{Ligand,\ exp} / m_{Ligand,theor}) * 100$$

5) Limitations

This model is the simplest method for estimate the coating rate of the particle but has however several limitations:

- ➔ The formula giving the concentration of the Ti sites at the surface as a function of the particle size and the TiO_2 concentration is for the case of an anatase TiO_2 NPs.
- ➔ The calculation of surface sites were done taking into account the case of primary particles perfectly dispersed. However, experimentally, we observe the presence of agglomerates of several particles which decrease the surface area and therefore the concentration of Ti and O sites available at the surface.
- ➔ The Ti / O ratio at the surface is evaluated according to the (001) plane of the anatase lattice of TiO_2. This ratio may depend on the surface and the distribution of the atoms in other plans, the presence of defects.
- ➔ In the case of CellTak®, the adhesion mechanism is unknown.
- ➔ We also did not taken into account the steric hindrance of the different ligands and the matter of the accessibility to the different sites on the surface.