Supporting Information

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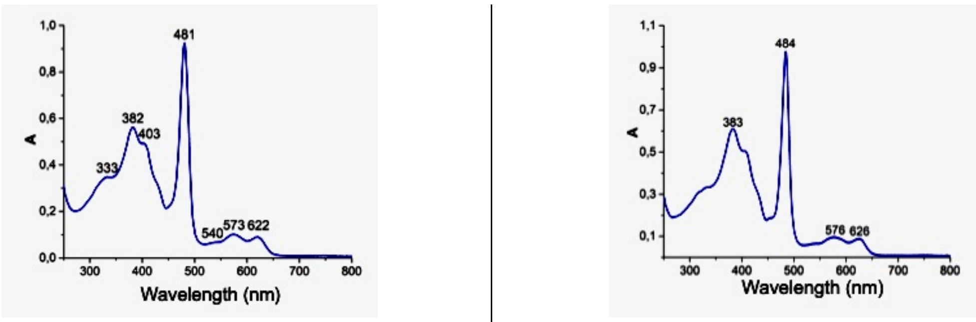
1. UV-vis and HRMS-ESI spectra of complexes Mn(TMPIC), Mn(TMPIP) and Mn(TMPIP-OH)



A B

Figure S1. UV-vis spectra of **Mn(TMPIC)** (a) and **Mn(TMPIP)** (b) in chloroform solution.

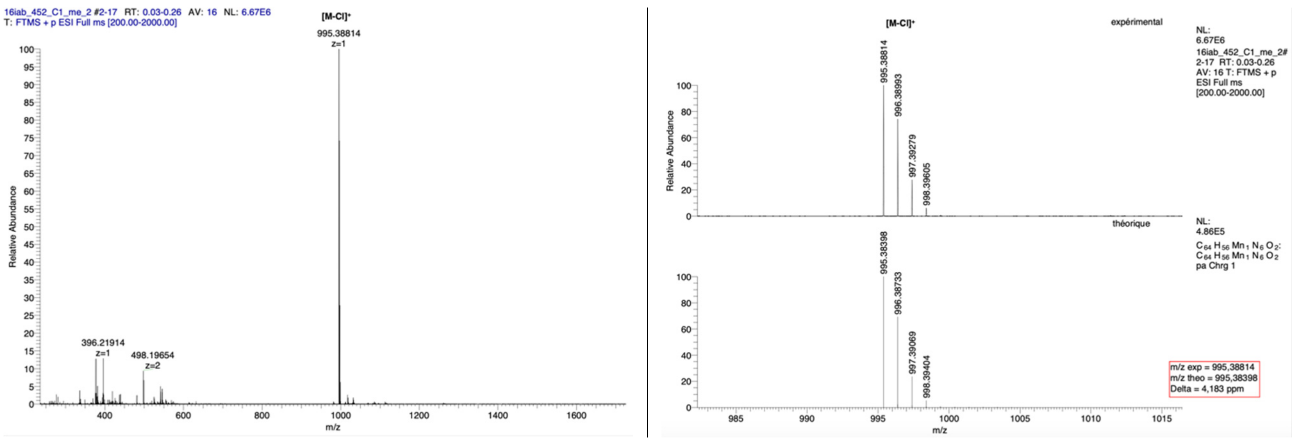


Figure S2. HRMS-ESI mass spectrum of **Mn(TMPIC)**.

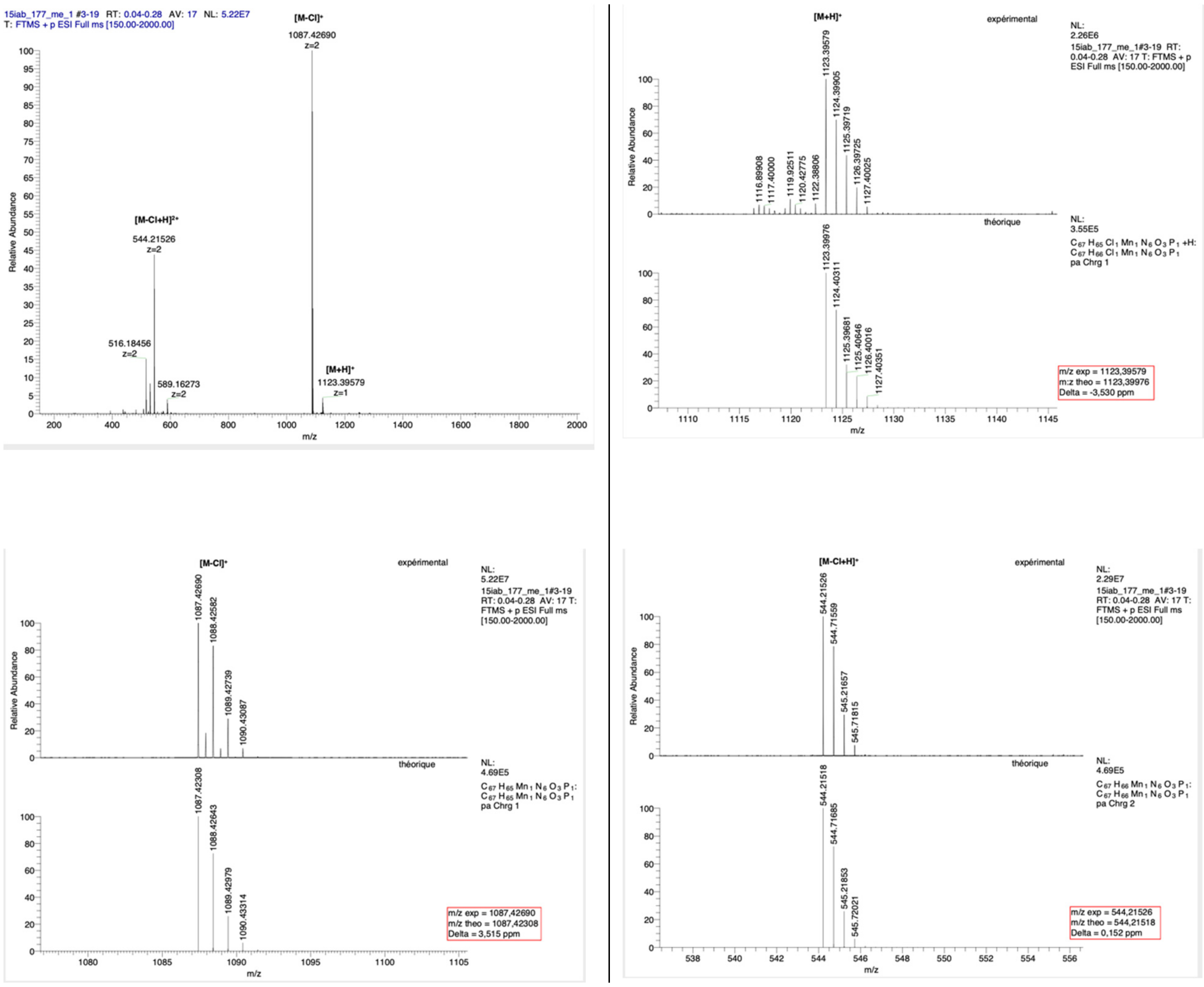


Figure S3. HRMS-ESI mass spectrum of **Mn(TMPIP)**.

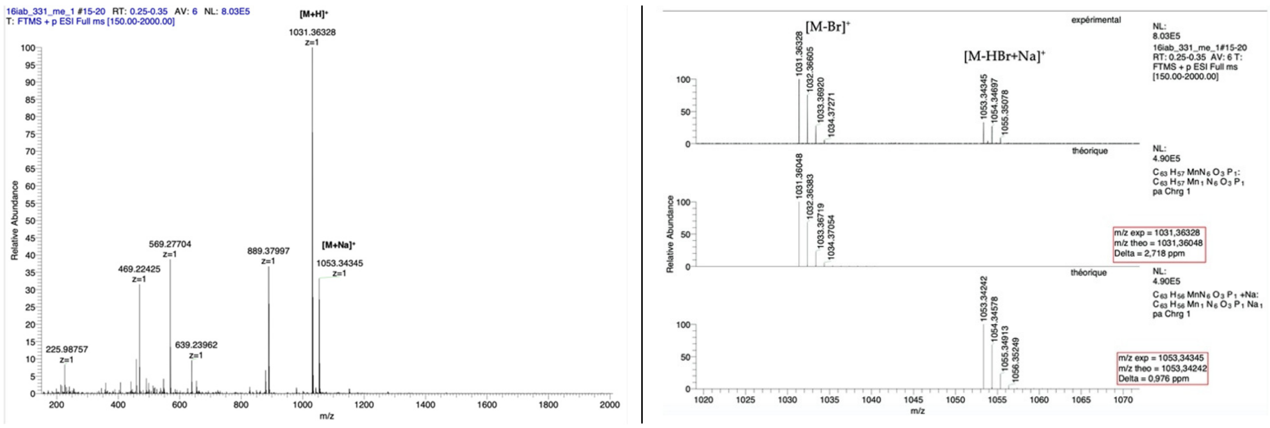
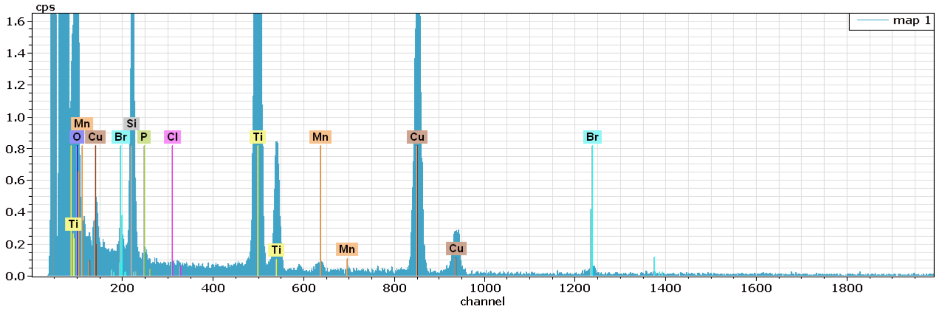
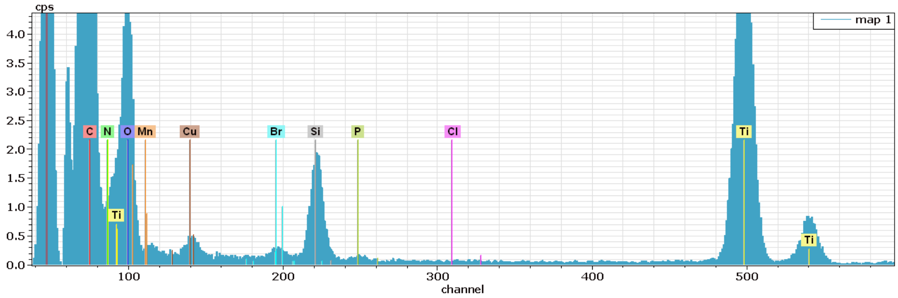


Figure S4. HRMS-ESI mass spectrum of **Mn(TMPIP-OH)**.

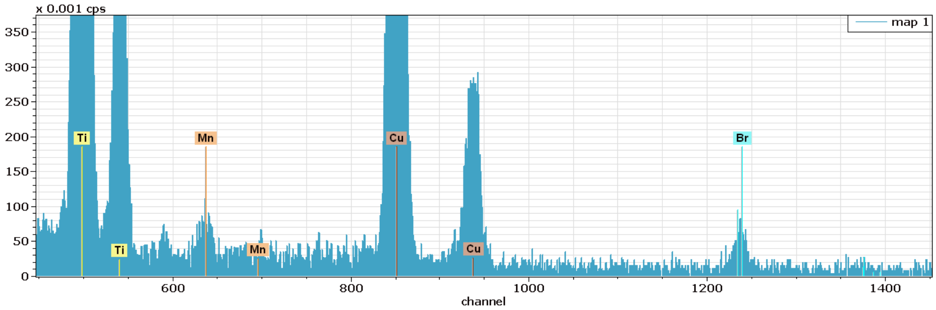
2. Studies of chemical composition of hybrid materials



(a)



(b)



(c)

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
O	8	K-series	55.51	55.51	79.00	1.3
P	15	K-series	0.32	0.32	0.23	0.0
Cl	17	K-series	0.06	0.06	0.04	0.0
Ti	22	K-series	42.52	42.52	20.22	0.9
Mn	25	K-series	0.40	0.40	0.17	0.1
Br	35	K-series	1.19	1.19	0.34	0.1
		Total:	100.00	100.00	100.00	

(d)

Figure S5. EDX spectra in STEM mode of hybrid material **Mn(TMPIP)/TiO_2**: all studied region (a), the region of 0–0.6 keV (b) the region of 0.6–1.4 keV (c), the results of quantitative analysis (d). Cu is observed because of spurious X-rays coming from the TEM copper grid.

Table S1. Chemical composition of solids prepared by grafting **Mn(TMPIP)** and **Mn(TMPIC)** [1].

Entry	Material	Calculated formula		Elemental analysis						
				C/N	N/P	Ti/P	Ti/N	Ti/Mn	N/Mn	P/Mn
1	**Mn(TMPIP)/TiO_2**		found	14.6	6.2	113.4	18.4	140.2	7.61	1.24
		$(C_{63}H_{55}N_6PMnBrO_2)(TiO_2)_{125}(H_2O)_{175}(C_3H_7OH)_8$	calcd.	15.8	6.0	125.0	20.8	125.0	6.0	1.0
2	**Mn(TMPIP)/TiO_2-1**		found	11.2	5.3	25.8	4.9	29.1	6.0	1.1
		$(C_{63}H_{55}N_6PMnBrO_2)(TiO_2)_{28}(H_2O)_{46}$	calcd.	10.5	6.0	28.0	4.7	28.0	6.0	1.0
3	**Mn(TMPIC)/TiO_2**		found	12.9	-	-	16.0	106.7	6.7	-
		$(C_{64}H_{55}N_6PMnClO_2)(TiO_2)_{100}(H_2O)_{146}(C_3H_7OH)_4$	calcd.	13.3	-	-	16.7	100.0	6.0	-
4[a]	**Mn(TMPIC)/TiO_2-1**		found	10.9	-	-	4.8	34.6	7.8	-
		$(C_{64}H_{55}N_6PMnClO_2)(TiO_2)_{32}(H_2O)_{45}(C_3H_7OH)_3$	calcd.	12.0	-	-	5.3	32.0	6.0	-

[1] Calculation were made using the data of C, N and H analyses (Thermo Electron Flash EA 1112 analyser) and P, Ti and Mn analyses (ICP-OES ICAP 7400 instrument).

3. FTIR spectra of hydride materials and referenced compounds

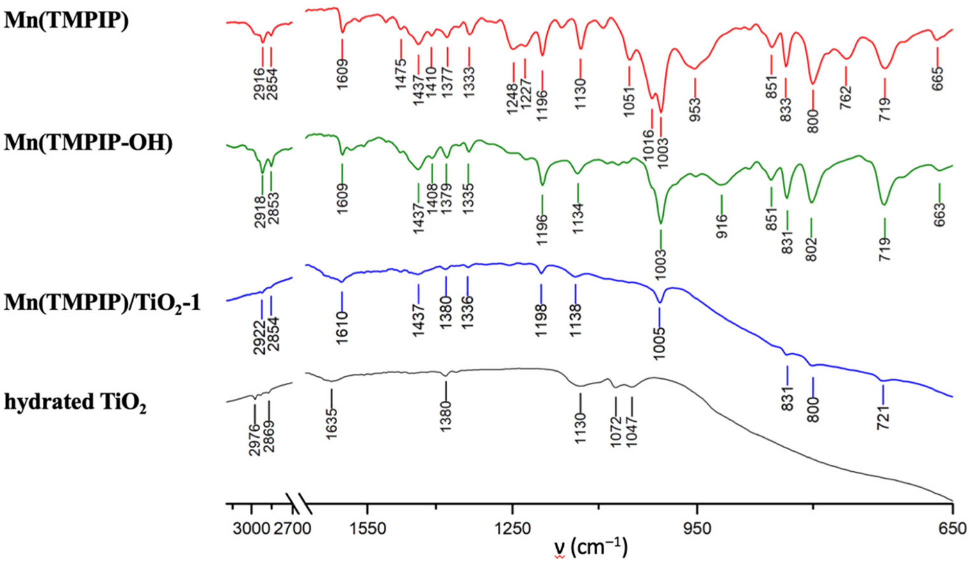


Figure S6. FTIR spectra of **Mn(TMPIP)**, **Mn(TMPIP-OH)**, **Mn(TMPIP)/TiO_2-1** and hydrated TiO_2.

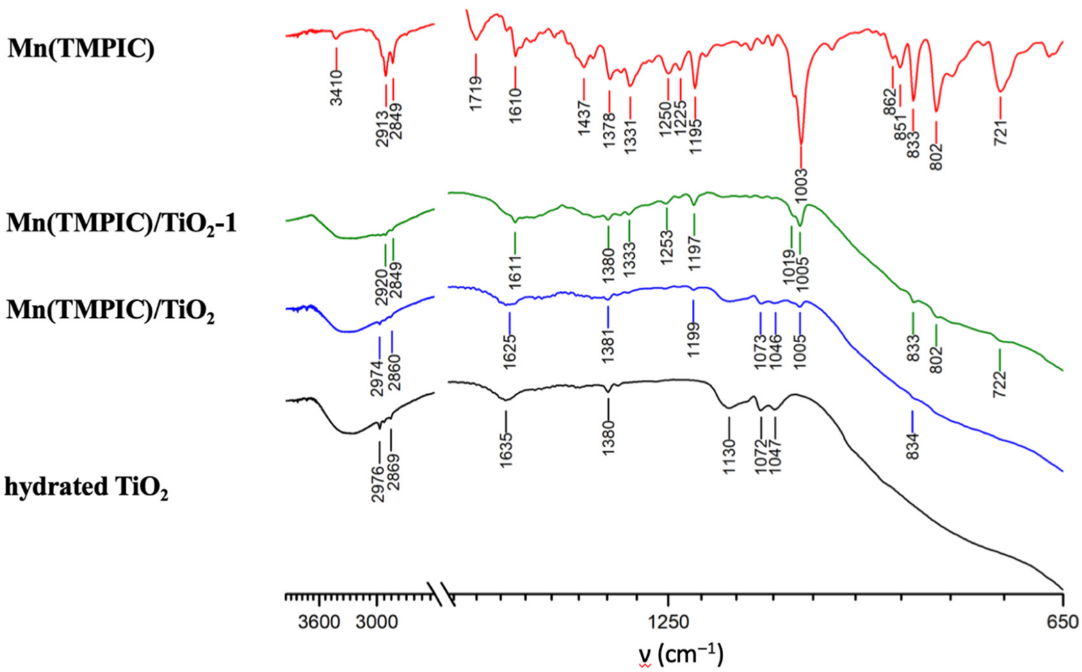
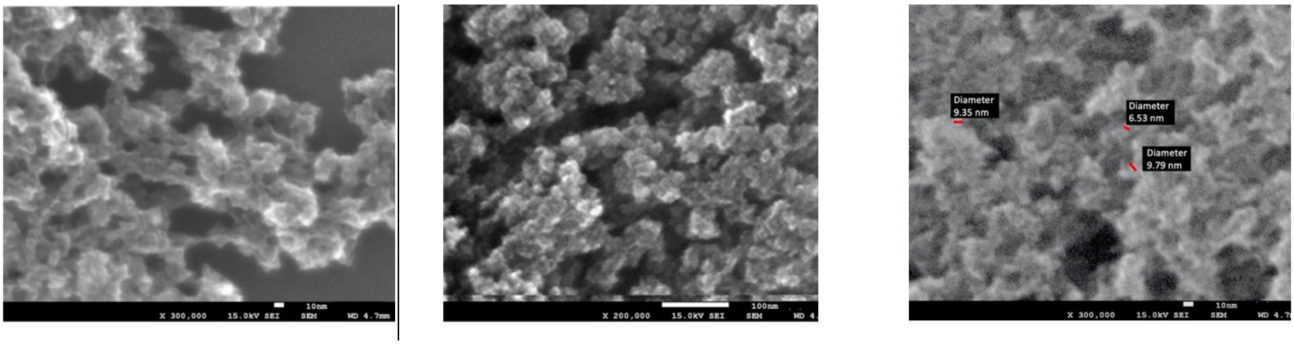


Figure S7. FTIR spectra of **Mn(TMPIC)**, **Mn(TMPIC)/TiO_2-1**, **Mn(TMPIC)/TiO_2**, and hydrated TiO_2.

4. Characterization of porosity and morphology of hybrid materials

Table S2. BET surface area, total pore volume and pore diameter for hydrated titania and heterogenized catalysts obtained in this work.

Entry	Solid	BET surface area [$m^2\ g^{-1}$]	Total pore volume [$m^3\ g^{-1}$]	Pore diameter [Å]
1	**TiO_2**	705	1.25	20–150
1	**Mn(TMPIP)/TiO_2**	575	0.88	20–100
2	**Mn(TMPIP)/TiO_2-1**	291	0.44	20–80
3	**Mn(TMPIC)/TiO_2**	429	0.83	20–150
5	**Mn(TMPIC)/TiO_2-1**	312	0.55	20–120



a) b)

FigureS8. SEM microphotographs of (a) bare hydrated TiO_2, and (b) **Mn(TMPIP)/TiO_2**.

5. Hot filtration test for oxidation of thioanisole catalyzed by Mn(TMPIP)/TiO_2

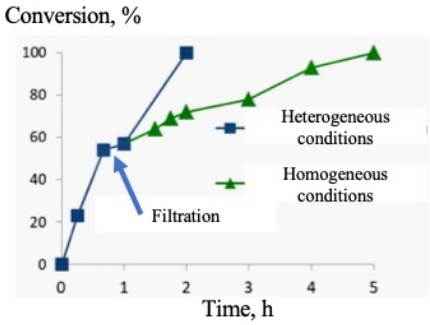
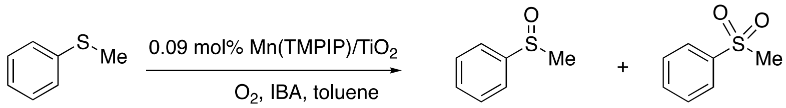


Figure S9. The hot filtration test for oxidation reaction of thioanisole with molecular oxygen in the presence of **Mn(TMPIP)/TiO_2** and IBA (Table 2, entry 1).

6. Recycling of Mn(TMPIP)/TiO_2

Table S3. Recycling of **Mn(TMPIP)/TiO_2** [1].



Entry	Time (h)	Conversion[2] (%)	Selectivity[2] (%)		Mn content[3] (ppm)
			Sulfoxide	Sulfone	
1	3	100	98	2	< 5
2	4	95	99	1	< 5
3	4.5	92	99	1	< 5
4	5.5	97	99	1	< 5
5	3	98	99	1	< 5
6	3.5	98	98	2	< 5
7	4.5	100	96	4	< 5

[1] Reaction conditions: 2.5 mmol of tioanisole, molecular oxygen (1 atm), IBA (5 equiv.), 0.09 mol% of heterogenized complex (calculations were based on the data of ICP analysis of **Mn(TMPIP)/TiO_2**), toluene (10 mL) were stirred at given temperature under O_2 (1 atm). Reaction time required for complete thioanisole oxydation was change non-systematically in these experiments that can be probably explain by difference in stirring of these heterogeneous reactions. [2] Conversion and selectivity were determined by GC-MS analysis of reaction mixtures. Naphthalene was used as an internal standard. [3] Manganese content was determined by ICP-OEP.

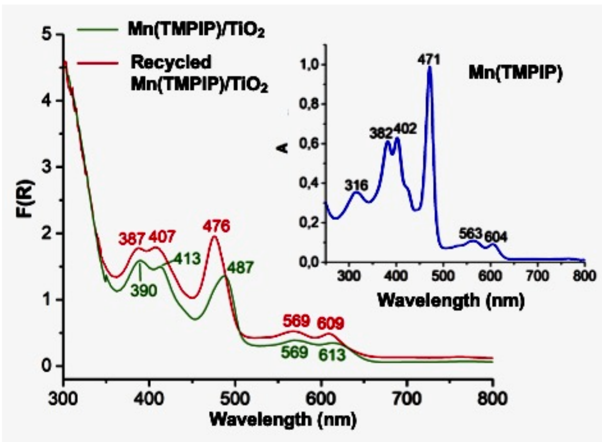


Figure S10. Kubelka-Munk transformed diffusion reflectance spectra of **Mn(TMPIP)/TiO_2** before and catalytic tests. The solid recovered after the 7th catalytic cycle was analysed. The electronic absorption spectrum of complex **Mn(TMPIP)** in methanol is shown on the inlet.