Supplementary Information (SI) for Catalysis Science & Technology.

Microwave-assisted aqueous MMA polymerization over TiO_2 nanotubes decorated with vanadium complexes

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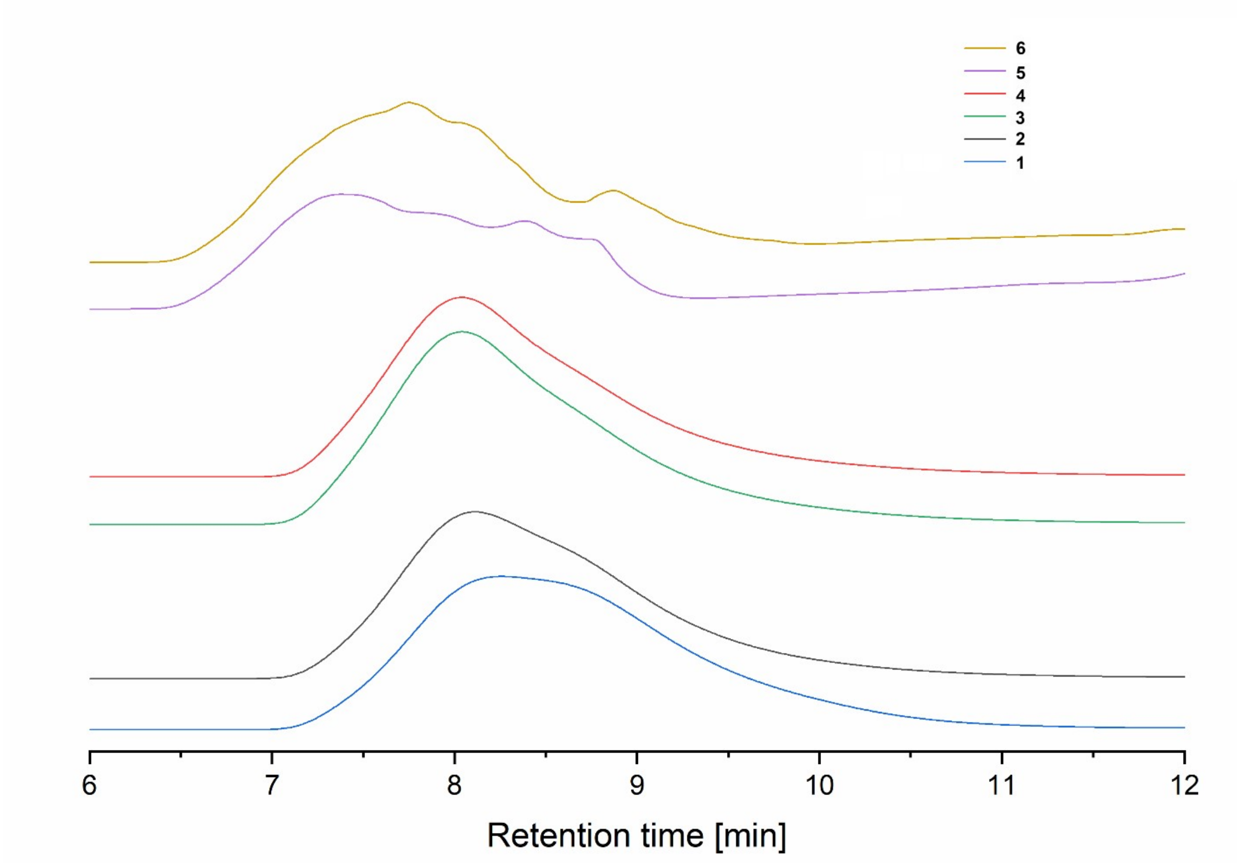


Figure S1. GPC chromatogram for PMMA samples obtained using different conditions and catalysts: 1 - VO(dipic)(bipy)[a], 2 - VO(dipic)(phen)[a] , 3 - VO(dipic)(bipy)/TiO_2[a], 4 - VO(dipic)(phen)/TiO_2[a], 5 - VO(dipic)(bipy)/TiO_2[MW], 6 - VO(dipic)(phen)/TiO_2[MW]. [a]Conditions: precatalyst (3 μmol), 1500eq. Et_2AlCl (activator), 1 mL DMSO, 1 mL toluene, 1 atm; [MW]Conditions: microwave, aqua, 80 °C, 150 W, 2 bar, 15 minutes, 1.5mL MMA.

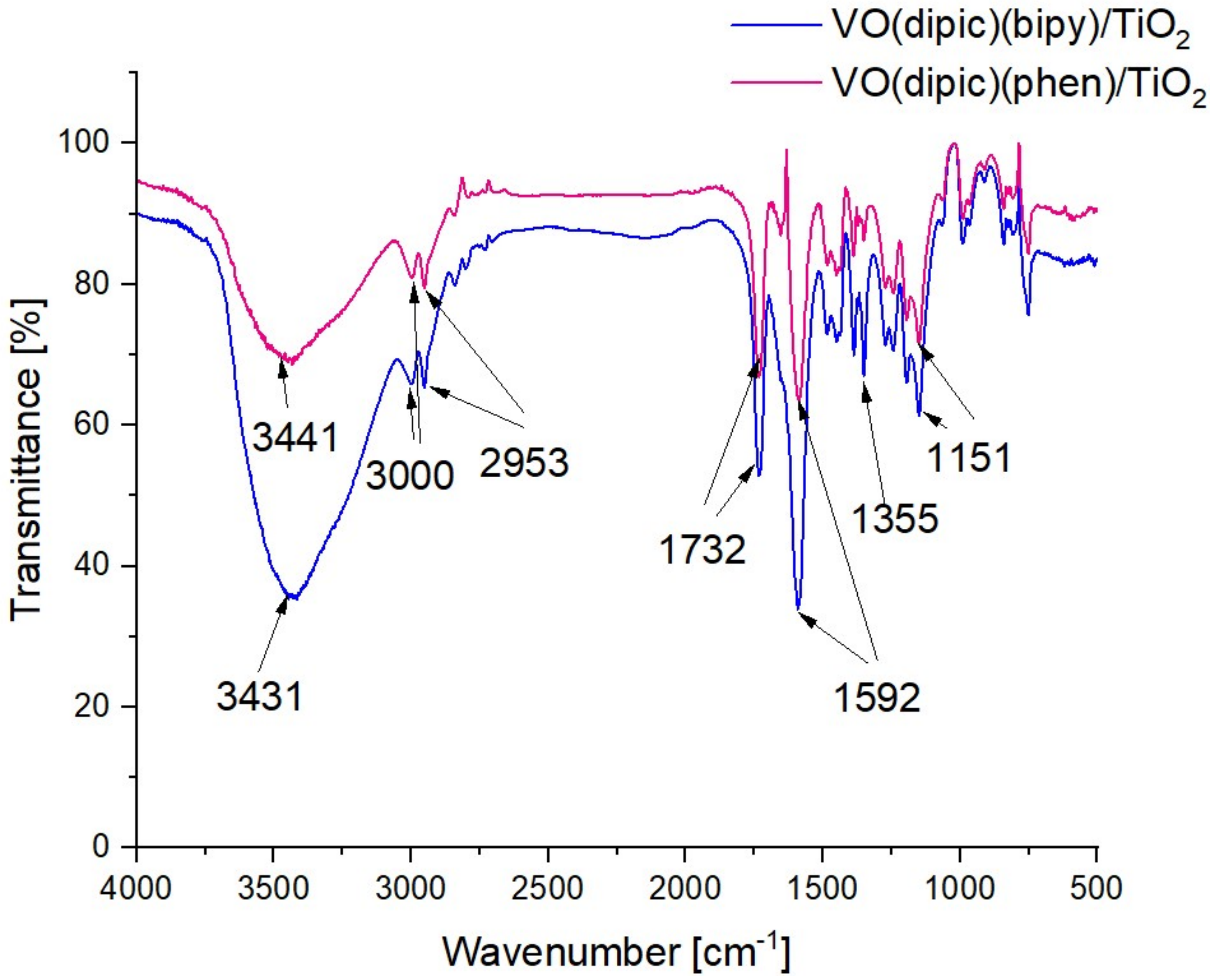


Figure S2. FT-IR spectra for PMMA obtained using VO(dipic)(phen)\$TiO_2$ and VO(dipic)(bipy)\$TiO_2$ in aqueous solution (microwave; 80 °C)

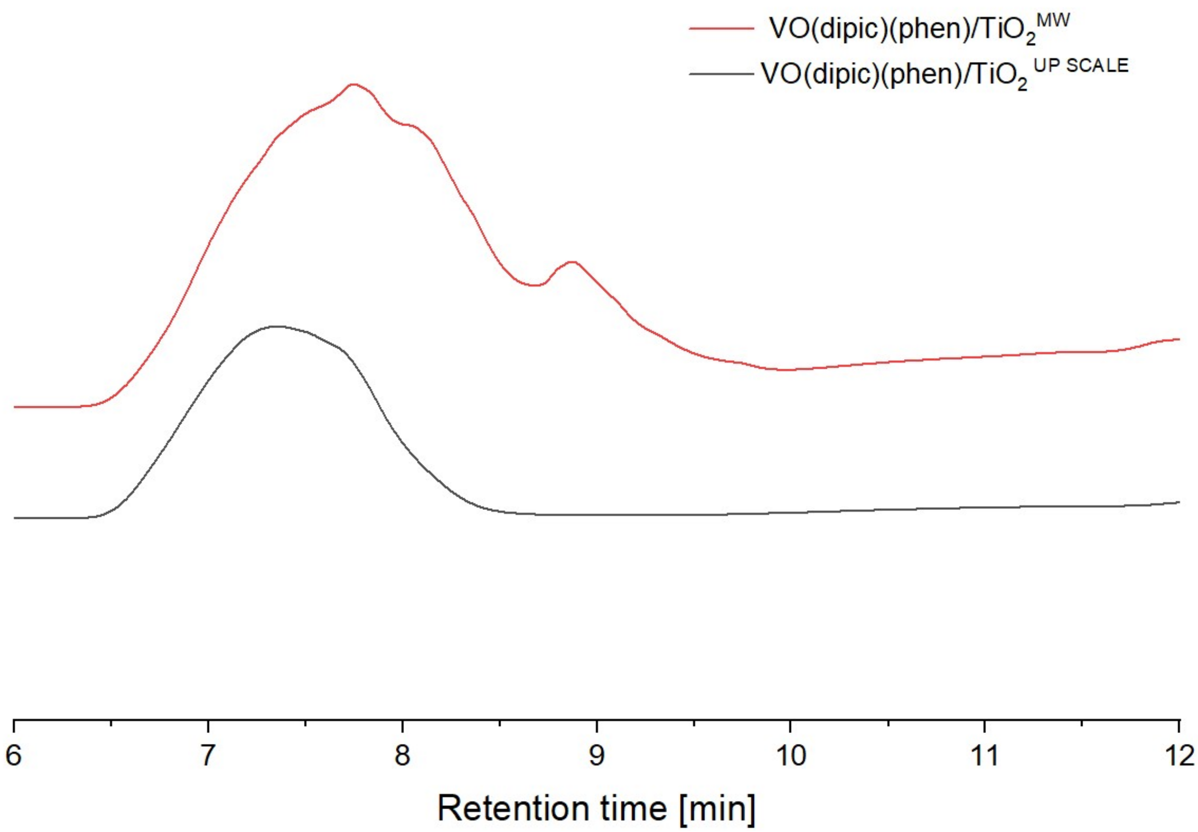


Figure S3. GPC chromatograms for PMMA samples obtained using VO(dipic)(phen)\TiO_2 and in aqueous solution (microwave; up-scale).

Table S1. The summary of the number (Mn) and weight (Mw) average molecular weights and polydispersity (PDI) of PMMA samples.

Catalyst	Mn (Da)	Mw (Da)	PDI (-)
VO(dipic)(phen)/TiO_2^{MW}	536 916	903 506	1.68
	125 645	127 987	1.02
	39 389	40 198	1.02
VO(dipic)(phen)/$TiO_2^{UP\ SCALE}$	429 289	1 239 241	2.88

Table S2. XPS study results of samples before being used as catalysts.

Catalyst	Region	Assignment	Binding Energy [eV]	FWHM [eV]	Atomic Conc. [%]
VO(dipic)(bipy)/TiO_2	V 2p3	V(IV)	516.06	1.49	0.49
		V(V)	517.08	1.49	0.87
	Ti 2p3	Ti(IV) - TiO_2	458.8	1.15	15.93
	O 1s	Oxide (TiO_2)	529.93	1.19	27.96
		Oxide V-O	530.84	1.7	9.74
		C=O	532.09	1.7	7.69
	N 1s	Pyridinic N	399.94	1.6	3.15
		Pyridine N-oxide	401.84	1.6	0.4
	C 1s	Csp^2	284.3	1.14	4.72
		Csp^3	285	1.14	13.55
		C-N / C-O	286.1	1.63	9.29
		O=C-O	288.4	1.51	5.72
	K 2p3	K^+	292.8	1.15	0.49
VO(dipic)(phen)/TiO_2	V 2p3	V(IV)	515.94	1.4	0.95
		V(V)	517.24	1.49	1.36
	Ti 2p3	Ti(IV) - TiO_2	458.76	1.09	11.04
	O 1s	Oxide (TiO_2)	529.96	1.18	22.4
		Oxide V-O	530.88	1.22	7.67
		C=O	531.79	1.4	8.11
	N 1s	Pyridinic N	399.5	1.48	4.4
		Pyridine N-oxide	401.23	1.76	0.56
	C 1s	Csp^2	284.3	1.3	8.28
		Csp^3	285.05	1.6	23.62
		C-N / C-O	286.04	1.4	4.55
		O=C-O	288.42	1.4	6.26
		π-π shake-up	291.69	1.38	0.8

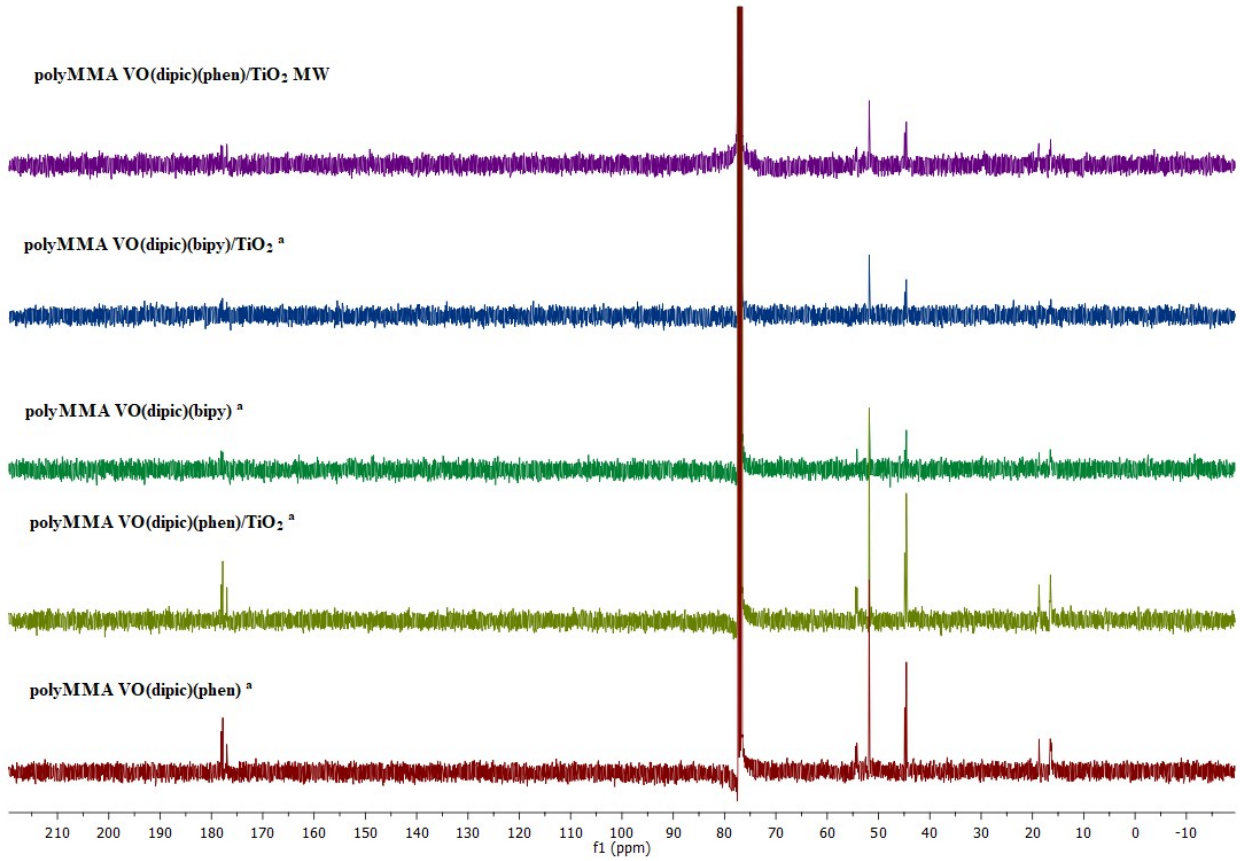


Figure S4. ^{13}C NMR spectra of PMMA. [a]Conditions: precatalyst (3 μmol), 1500eq. Et_2AlCl (activator), 1 mL DMSO, 1 mL toluene, 1 atm; [MW]Conditions: microwave, aqueous solution, 80 °C, 150 W, 2 bar, 15 minutes, 1.5mL MMA.

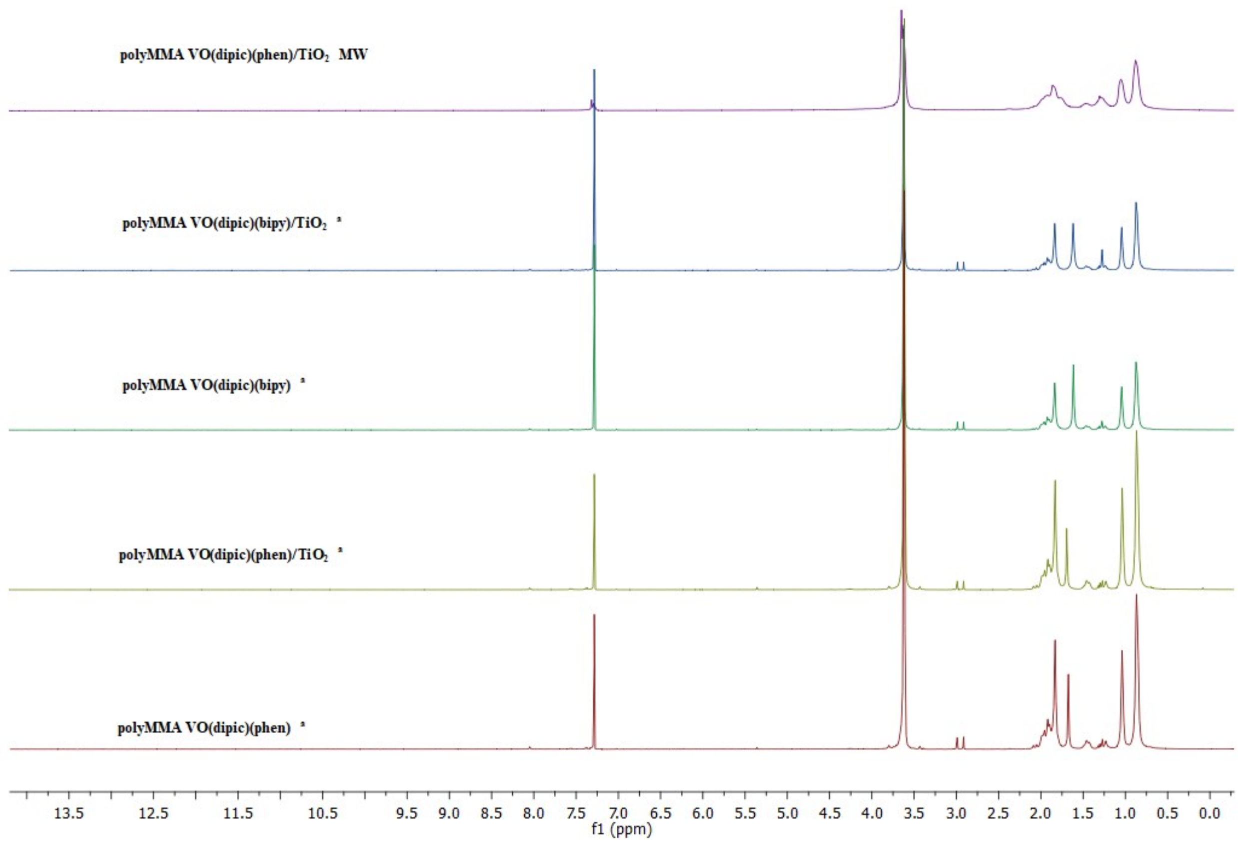


Figure S5. ^{1}H NMR spectra of PMMA. [a]Conditions: precatalyst (3 µmol), 1500eq. Et_2AlCl (activator), 1 mL DMSO, 1 mL toluene, 1 atm; **[MW]**Conditions: microwave, aqueous solution, 80 °C, 150 W, 2 bar, 15 minutes, 1.5mL MMA.

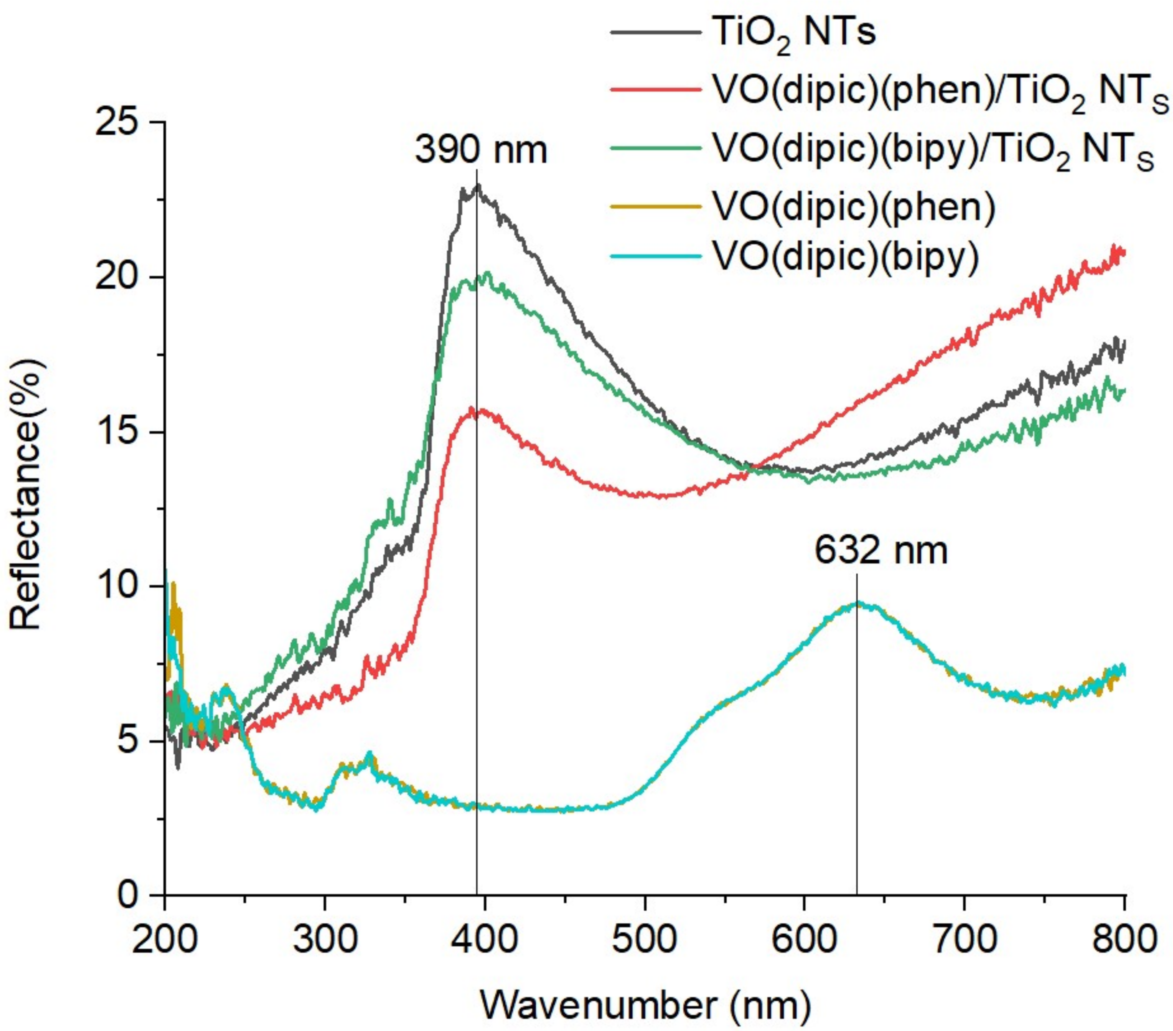


Figure S6. UV-Vis diffuse reflectance (DRS) spectra of the pristine TiO_2 NTs, pure vanadium(IV) coordination complexes, and the corresponding immobilized nanocomposites.

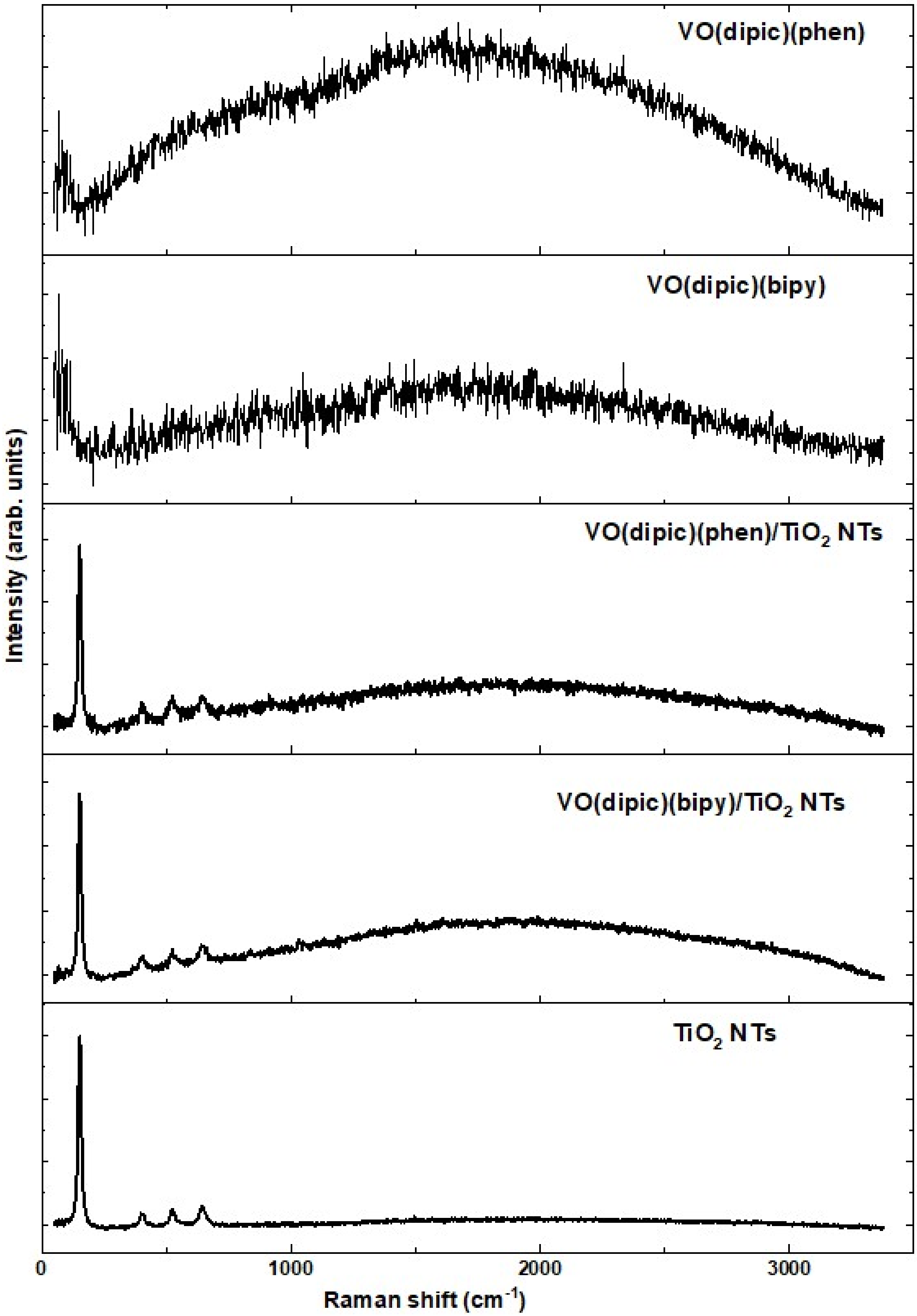
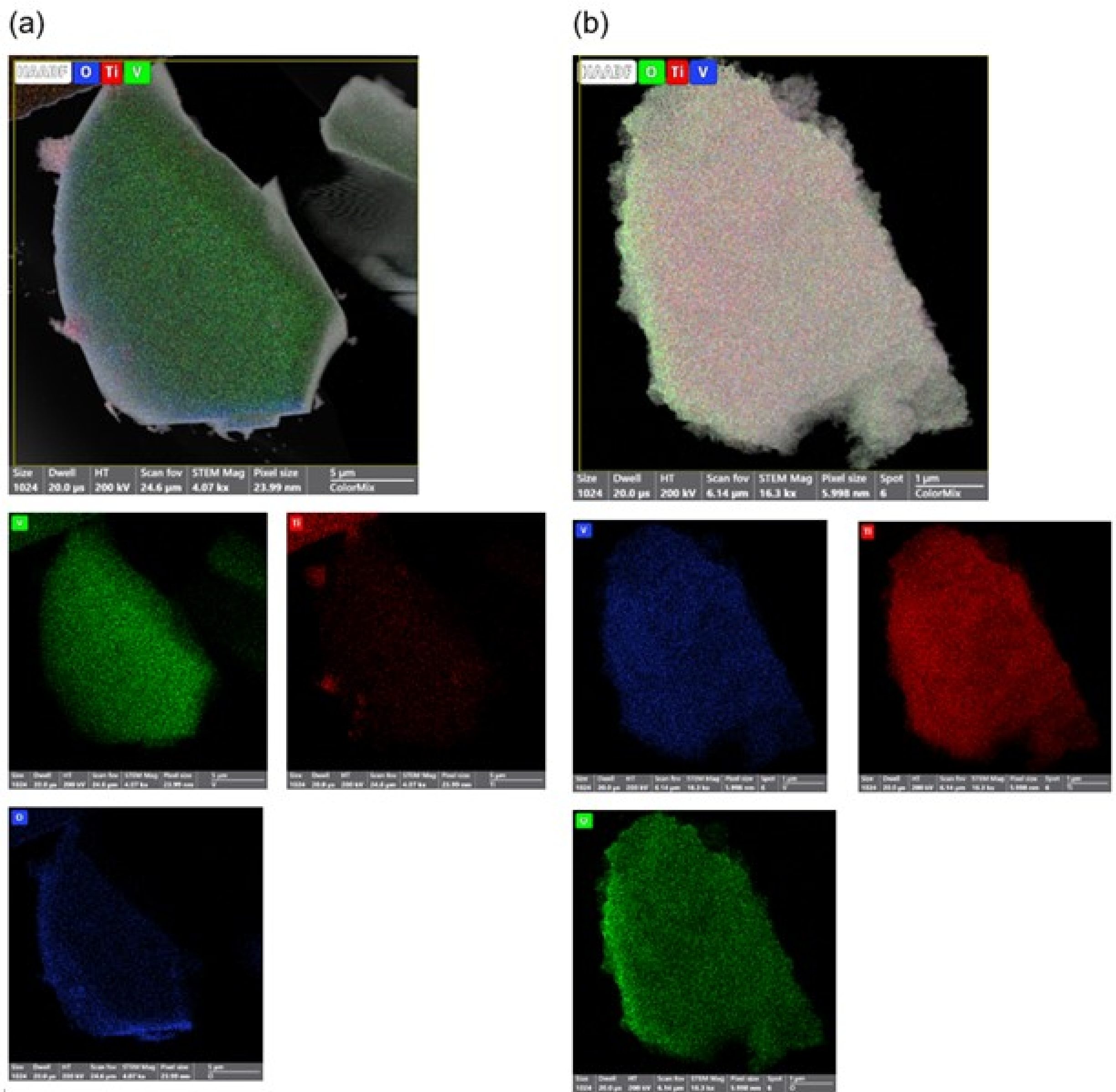


Figure S7. Raman spectra of the pristine TiO_2 NTs, pure vanadium(IV) coordination complexes, and the functionalized nanocomposites.

Table S3. Experimental sampling matrix for the optimization of microwave-assisted aqueous MMA polymerization.

Catalyst System	Method / Medium	Temp. [°C]	Time [min]	Pressure [bar]	SDS [mg]	Yield [mg]
VO(dipic)(bipy)	Conventional (Toluene/DMSO)	65	60	1	0	112
VO(dipic)(bipy)/TiO_2	Conventional (Toluene/DMSO)	65	60	1	0	151
VO(dipic)(phen)	Conventional (Toluene/DMSO)	65	60	1	0	150
VO(dipic)(phen)/TiO_2	Conventional (Toluene/DMSO)	65	60	1	0	198
VO(dipic)(bipy)/TiO_2	Microwave (Aqueous Emulsion)	80	15	2	100	619
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	15	2	100	854
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	5	2	100	120
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	10	2	100	500
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	20	2	100	880
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	30	2	100	895
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	20	15	2	100	110
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	40	15	2	100	420
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	60	15	2	100	710
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	90	15	2	100	860
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	15	2	25	250
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	15	2	50	400

VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	15	2	200	830
VO(dipic)(phen)/TiO_2	Microwave (Aqueous Emulsion)	80	15	1	100	690



(a)

Element	Atomic Fraction [at%]	Mass Fraction [wt%]
O	45.20	20.58
V	0.34	0.46
Ti	54.46	78.96

(b)

Element	Atomic Fraction [at%]	Mass Fraction [wt%]
O	46.18	22.10
V	0.39	0.59
Ti	53.43	77.31

Figure S8. EDS mapping for bipy (a) and phen (b) catalytic systems.