Supplementary Information

Surface interaction, polarity and probe mobility differences on organophosphonic acid modified titania: a spin probe EPR study

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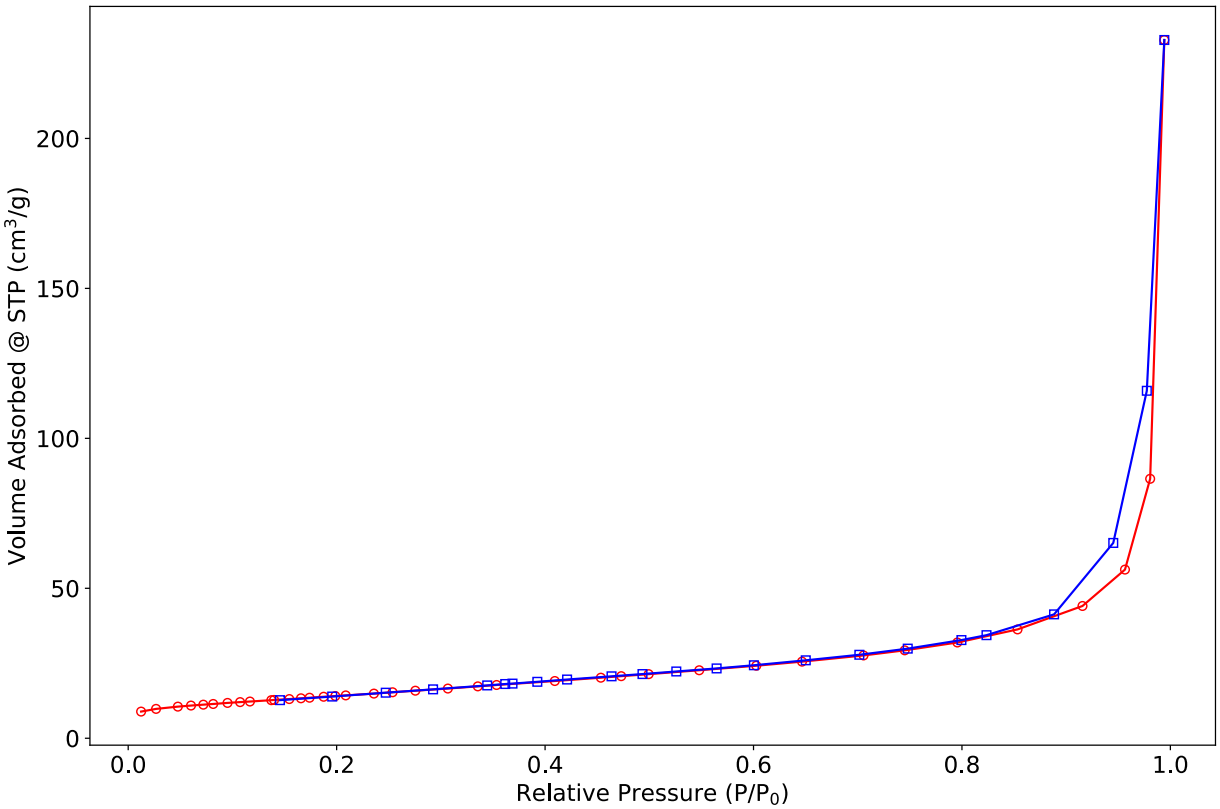


Figure S1. Nitrogen sorption isotherms of TiO_2 P25 measured at 77 K. The sample was degassed for 16 hours under a vacuum of around 0.02 mbar at 453 K before the measurement. Red: the adsorption curve; blue: the desorption curve.

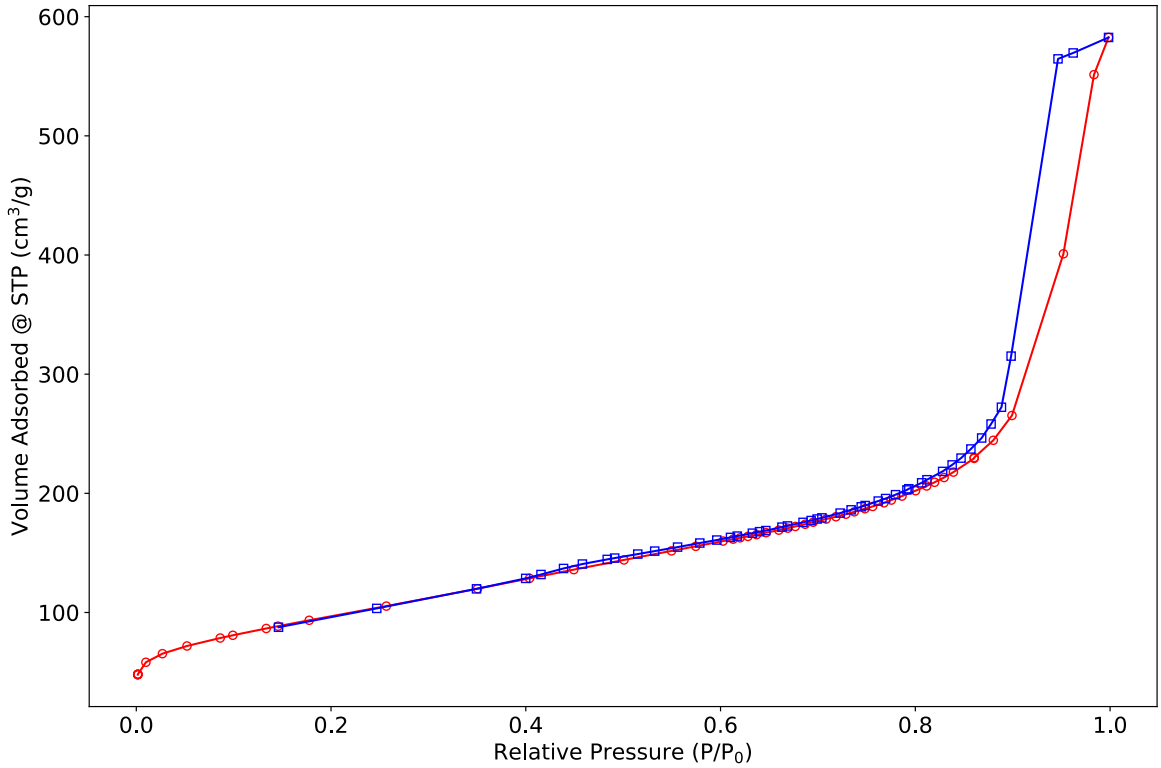
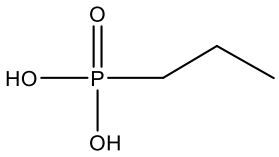
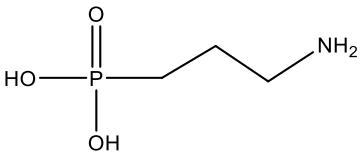


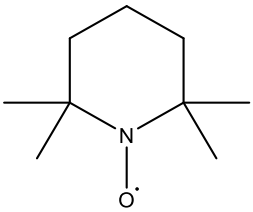
Figure S2. Nitrogen sorption isotherms of TiO_2 Hombikat M311 measured at 77 K. The sample was degassed for 16 hours under a vacuum of around 0.02 mbar at 453 K before the measurement. Red: the adsorption curve; blue: the desorption curve).



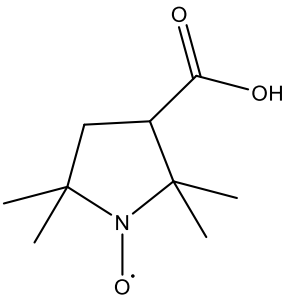
Propylphosphonic acid (PPA)



3-aminopropylphosphonic acid (3APPA)



(2,2,6,6-Tetramethylpiperidin-1-yl)oxy (TEMPO)



3-(carboxy)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (3CP)

Figure S3. Structural formulas of the PAs (PPA and 3APPA) and spin probes (TEMPO and 3CP) used in this work.

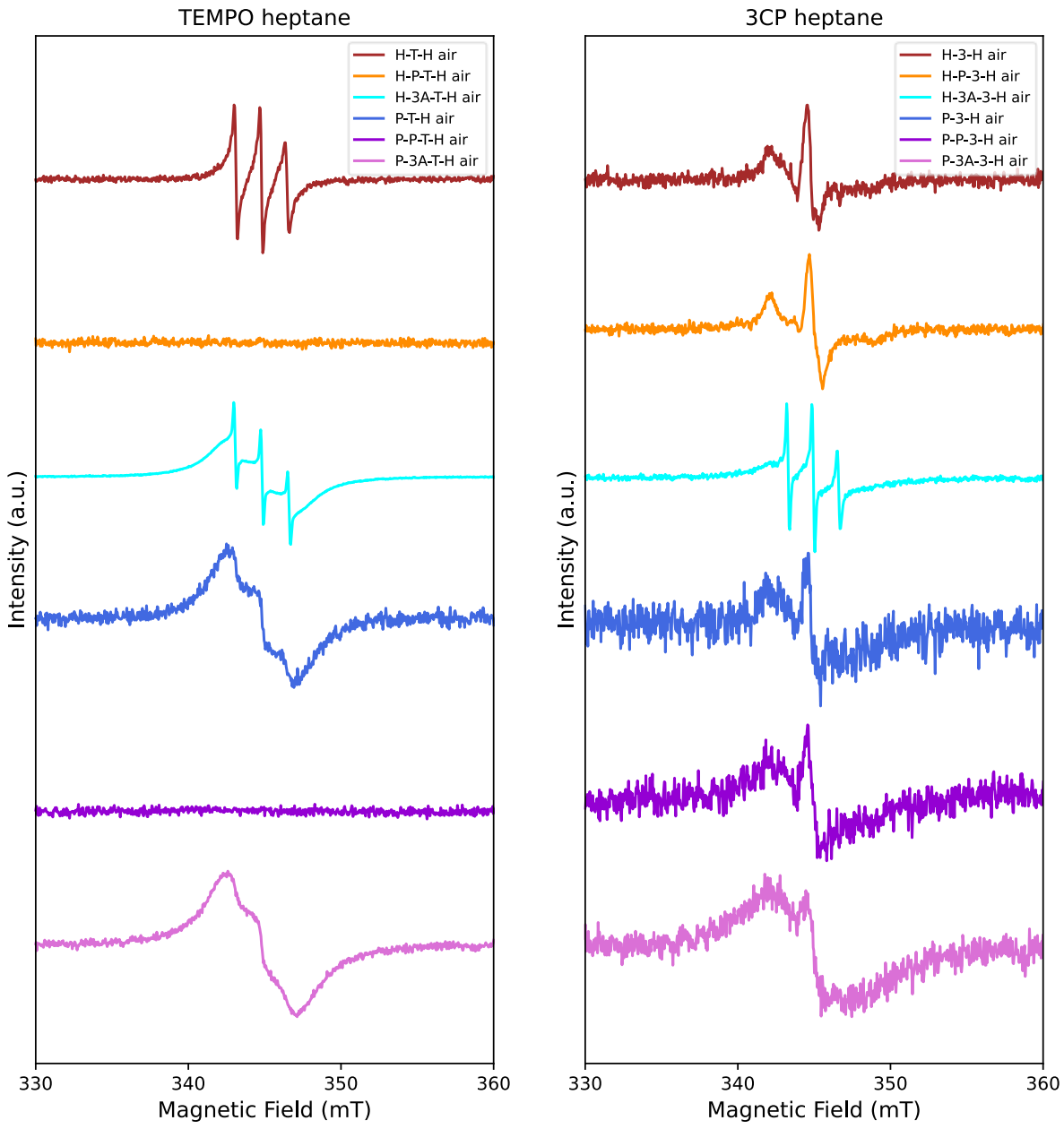


Figure S4. X-band cw-EPR spectra measured at room temperature before vacuum treatment (marked as "air") of TEMPO (left) and 3CP (right) adsorbed on unmodified, PPA- and 3APPA-modified TiO_2 Hombikat M311 and TiO_2 P25. Heptane was used as the solvent in the adsorption process. For sample labeling nomenclature: see section 2.2, main text.

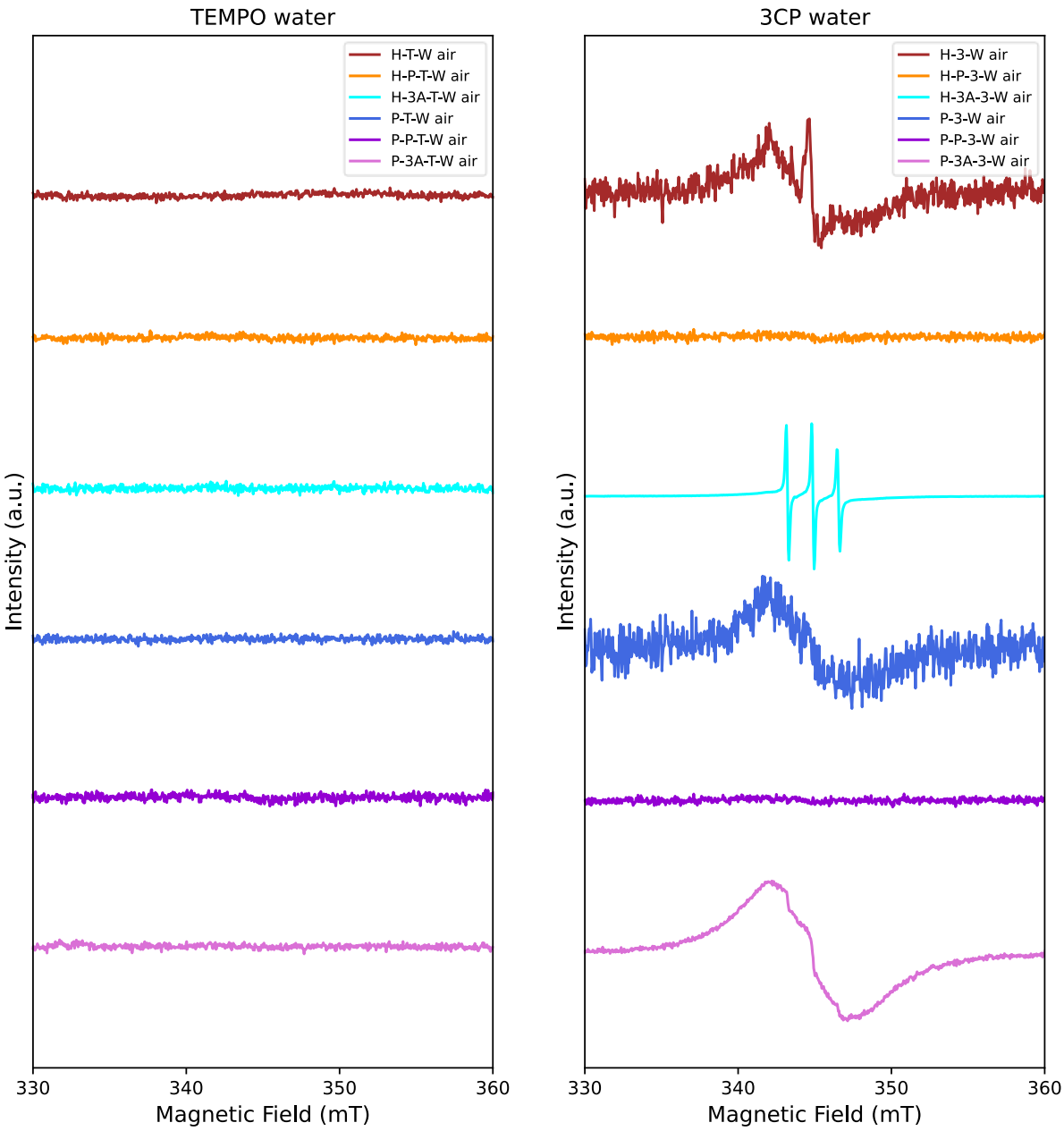


Figure S5. X-band cw-EPR spectra measured at room temperature before vacuum treatment (marked as "air") of TEMPO (left) and 3CP (right) adsorbed on unmodified, PPA- and 3APPA-modified TiO_2 Hombikat M311 and TiO_2 P25. Water was used as the solvent in the adsorption process. For sample labeling nomenclature: see section 2.2, main text.

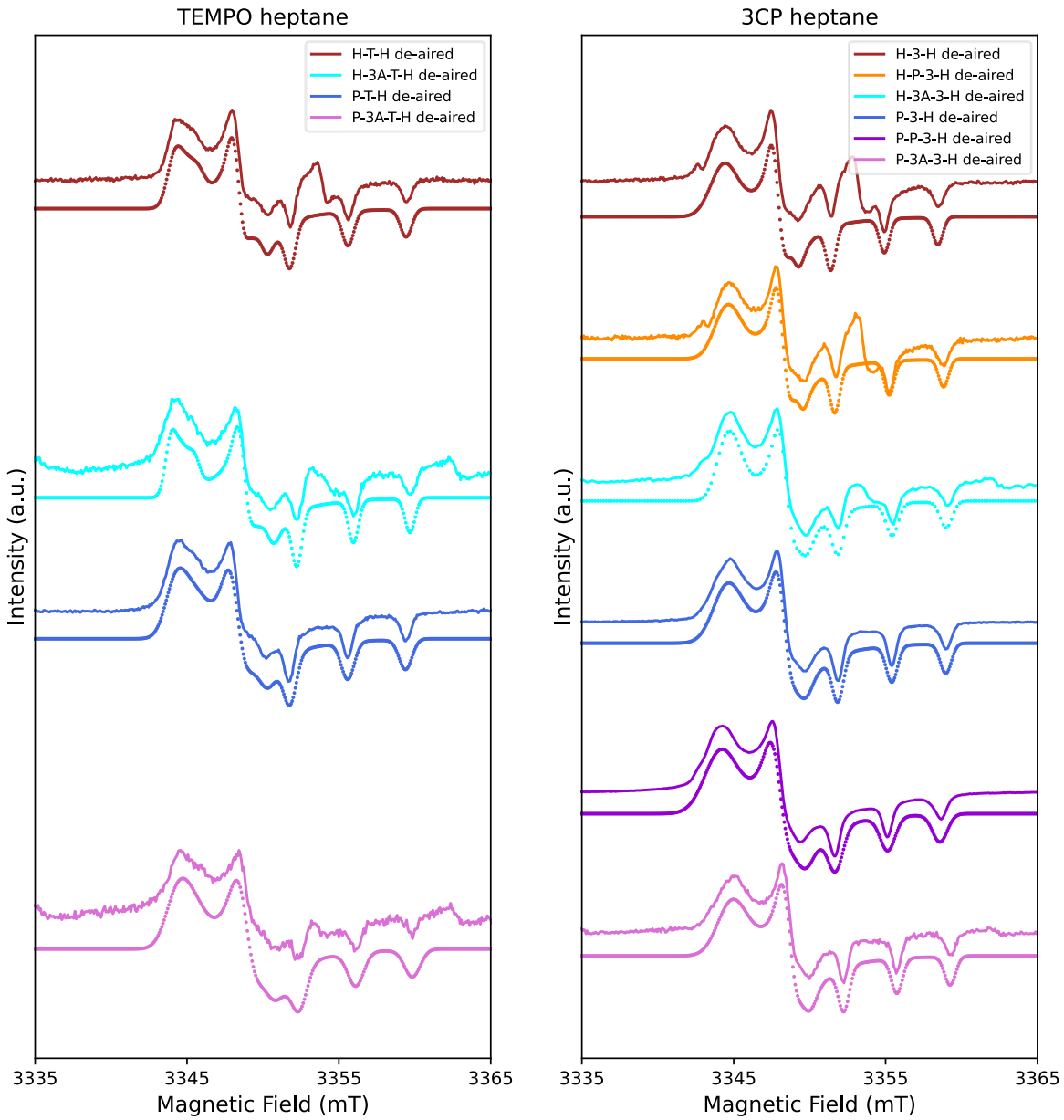


Figure S6. W-band cw-EPR spectra measured at 120 K after vacuum treatment (marked as "de-aired") of TEMPO (left) and 3CP (right) adsorbed on unmodified, PPA- and 3APPA-modified TiO_2 Hombikat M311 and TiO_2 P25. Heptane was used as the solvent in the adsorption process. Only contributions from the spin-probe molecules were included in the simulated spectra, which are shown just below the respective experimental spectra. For sample labeling nomenclature: see section 2.2, main text.

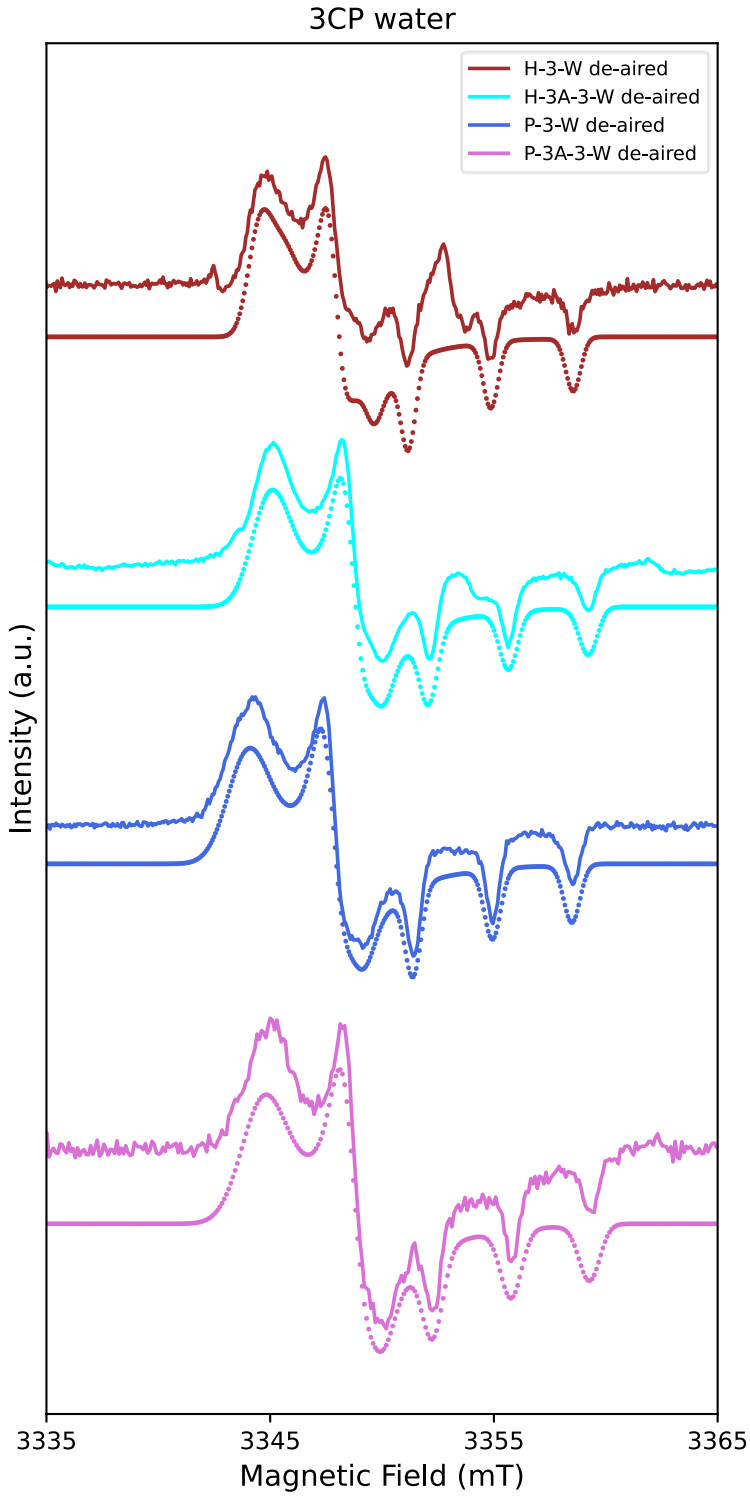


Figure S7. W-band cw-EPR spectra measured at 120 K after vacuum treatment (marked as "de-aired") of 3CP adsorbed on unmodified, and 3APPA-modified TiO_2 Hombikat M311 and TiO_2 P25. Water was used as the solvent in the adsorption process. Only contributions from the 3CP molecules were included in the simulated spectra, which are shown just below the respective experimental spectra. For sample labeling nomenclature: see section 2.2, main text.

*Table S1. The **g** and ^{14}N hyperfine (**A**) tensors of the spin probes on the surfaces of unmodified, PPA- and 3APPA-modified TiO_2 P25 and TiO_2 Hombikat M311 obtained from the simulations of the W-band cw-EPR spectra measured at 120 K (Figures 2, S6, and S7). The experimental error of the principal g and A values are estimated to be 0.00005 and 0.5 MHz, respectively.*

Spin probe	Surface	Solvent	g_x	g_y	g_z	A_x (MHz)	A_y (MHz)	A_z (MHz)
TEMPO	P25	chloroform	2.00861	2.00598	2.00216	20.6	20.6	106.4
		heptane	2.00863	2.00599	2.00216	20.6	20.6	106.3
	P25 3APPA	chloroform	2.00888	2.00593	2.00214	20.5	20.6	103.8
		heptane	2.00885	2.00595	2.00212	20.6	20.6	104.3
	Hombikat	chloroform	2.00857	2.00597	2.00217	20.6	20.5	107.0
		heptane	2.00856	2.00597	2.00218	20.5	20.5	107.0
	Hombikat 3APPA	chloroform	2.00887	2.00595	2.00215	20.5	20.5	104.3
		heptane	2.00890	2.00601	2.00217	20.5	20.6	103.9
3CP	P25	chloroform	2.00869	2.00605	2.00215	13.5	13.5	98.1
		heptane	2.00866	2.00603	2.00214	13.5	13.5	98.4
		water	2.00857	2.00606	2.00216	13.4	13.5	98.9
	P25 PPA	chloroform	2.00861	2.00601	2.00212	13.5	13.4	98.7
		heptane	2.00854	2.00603	2.00212	13.4	13.4	99.4
	P25 3APPA	chloroform	2.00874	2.00600	2.00212	13.3	13.4	97.4
		heptane	2.00876	2.00599	2.00212	13.3	13.4	97.3
		water	2.00872	2.00621	2.00232	13.4	13.5	97.9
	Hombikat	chloroform	2.00821	2.00596	2.00216	13.4	13.5	102.0
		heptane	2.00819	2.00597	2.00215	13.4	13.5	102.2
		water	2.00806	2.00590	2.00215	13.5	13.5	103.6
	Hombikat PPA	chloroform	2.00827	2.00591	2.00210	13.3	13.4	101.0
		heptane	2.00831	2.00593	2.00211	13.3	13.4	100.8
	Hombikat 3APPA	chloroform	2.00845	2.00601	2.00218	13.3	13.4	99.8
		heptane	2.00843	2.00600	2.00216	13.3	13.4	99.9
		water	2.00840	2.00597	2.00216	13.3	13.5	100.2

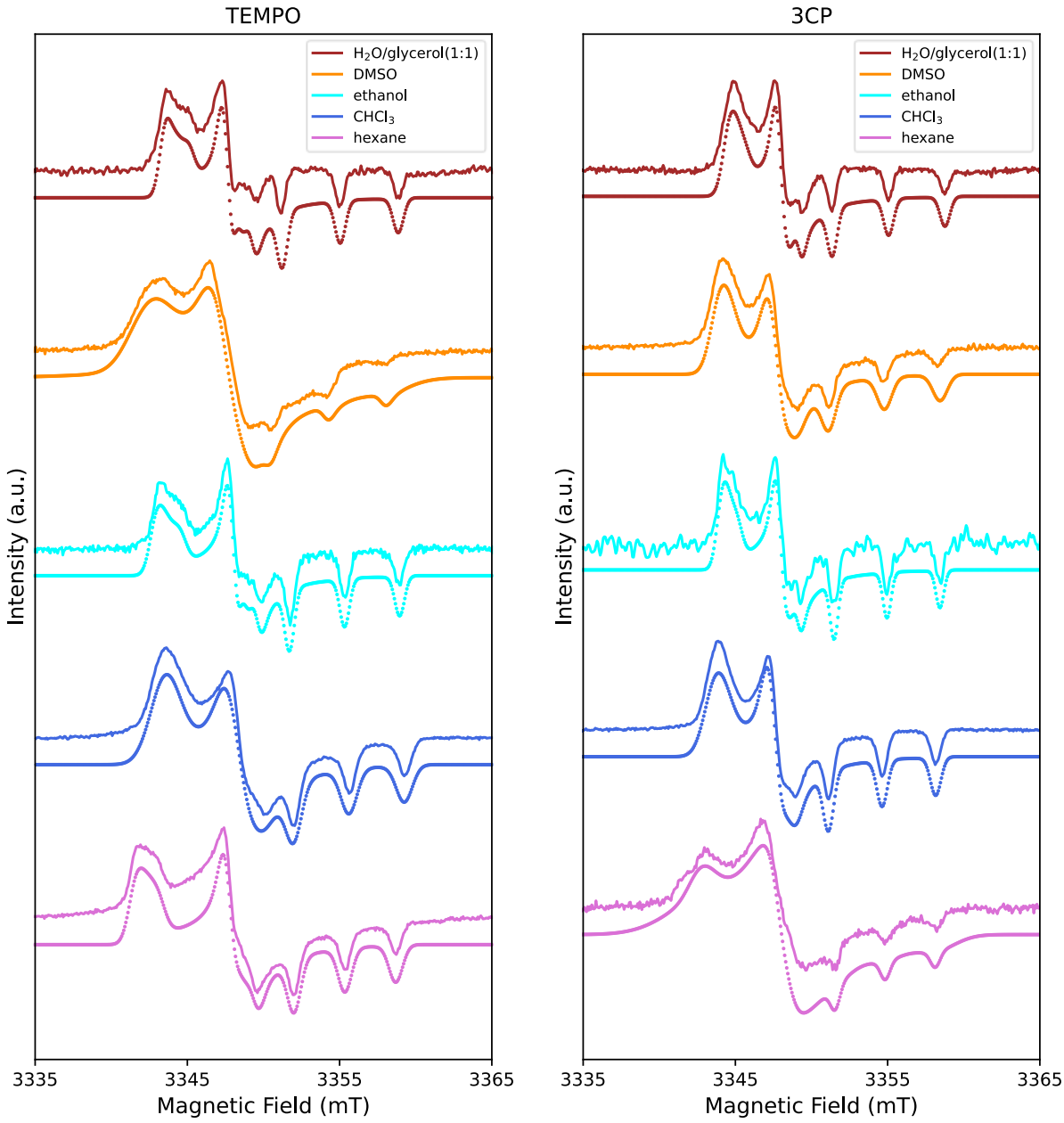


Figure S8. W-band cw-EPR spectra measured at 120 K of TEMPO (left) and 3CP (right) in several solvents: a mixture of water and glycerol (1:1), DMSO, ethanol, $CHCl_3$, and hexane. The simulated spectra are shown just below the respective experimental spectra. For sample labeling nomenclature: see section 2.2, main text.

*Table S2. The **g** and ^{14}N hyperfine (**A**) of the spin probes in solutions obtained from the simulations of the W-band cw-EPR spectra measured at 120 K (Figure S8), the experimental error of the principal g and A values are estimated to be 0.00005 and 0.5 MHz, respectively.*

Spin probe	Solvent	g_x	g_y	g_z	A_x (MHz)	A_y (MHz)	A_z (MHz)
TEMPO	H_2O/glycerol(1:1)	2.00857	2.00607	2.00217	20.6	20.5	106.7
	DMSO	2.00902	2.00605	2.00216	20.5	20.5	105.9
	ethanol	2.00919	2.00611	2.00219	20.5	20.4	101.4
	chloroform	2.00933	2.00609	2.00218	20.5	20.5	102.5
	hexane	2.01012	2.00618	2.00221	20.5	20.5	93.4
3CP	H_2O/glycerol(1:1)	2.00807	2.00603	2.00212	13.4	13.4	103.1
	DMSO	2.00848	2.00609	2.00217	13.4	13.4	102.1
	ethanol	2.00850	2.00608	2.00218	13.4	13.5	99.5
	chloroform	2.00867	2.00608	2.00219	13.5	13.5	100.1
	hexane	2.00942	2.00607	2.00214	13.5	13.5	92.1

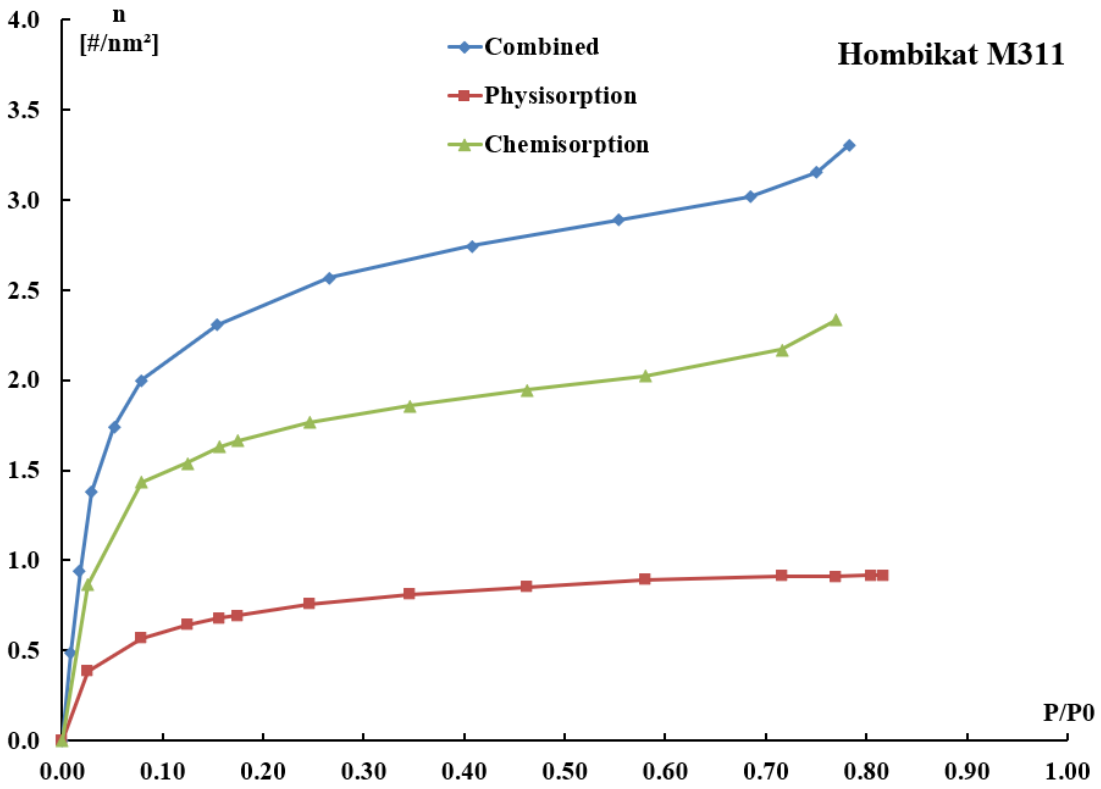


Figure S9. Two-cycle MeOH adsorption at 383 K on TiO_2 Hombikat M311 (top) and TiO_2 P25 (bottom). For the results of P25 please refer to Fig. S13 in [1]. The curves for combined and physisorption are based on measured values, whereas the chemisorption curve is derived by subtracting the physisorption data from the combined data (chemisorption + physisorption).

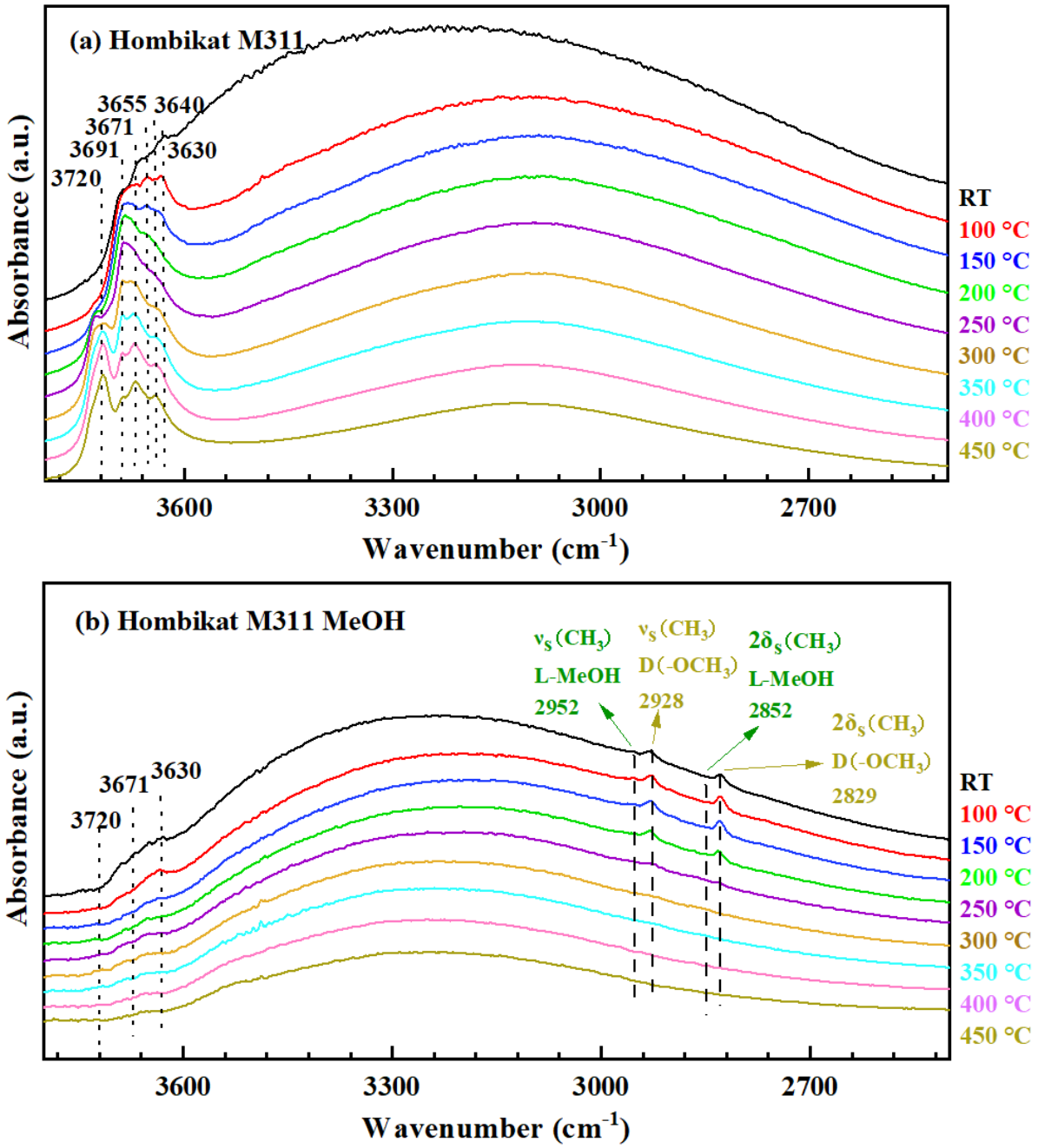


Figure S10. In-situ DRIFT spectra of Hombikat M311 (a) and measured after MeOH adsorption on Hombikat M311 (b), with increased temperatures under a constant Ar flow and against KBr as a background. For the spectra of P25 and MeOH chemisorbed P25 please refer to Fig. 1(a) and Fig. 4(a) in [1].

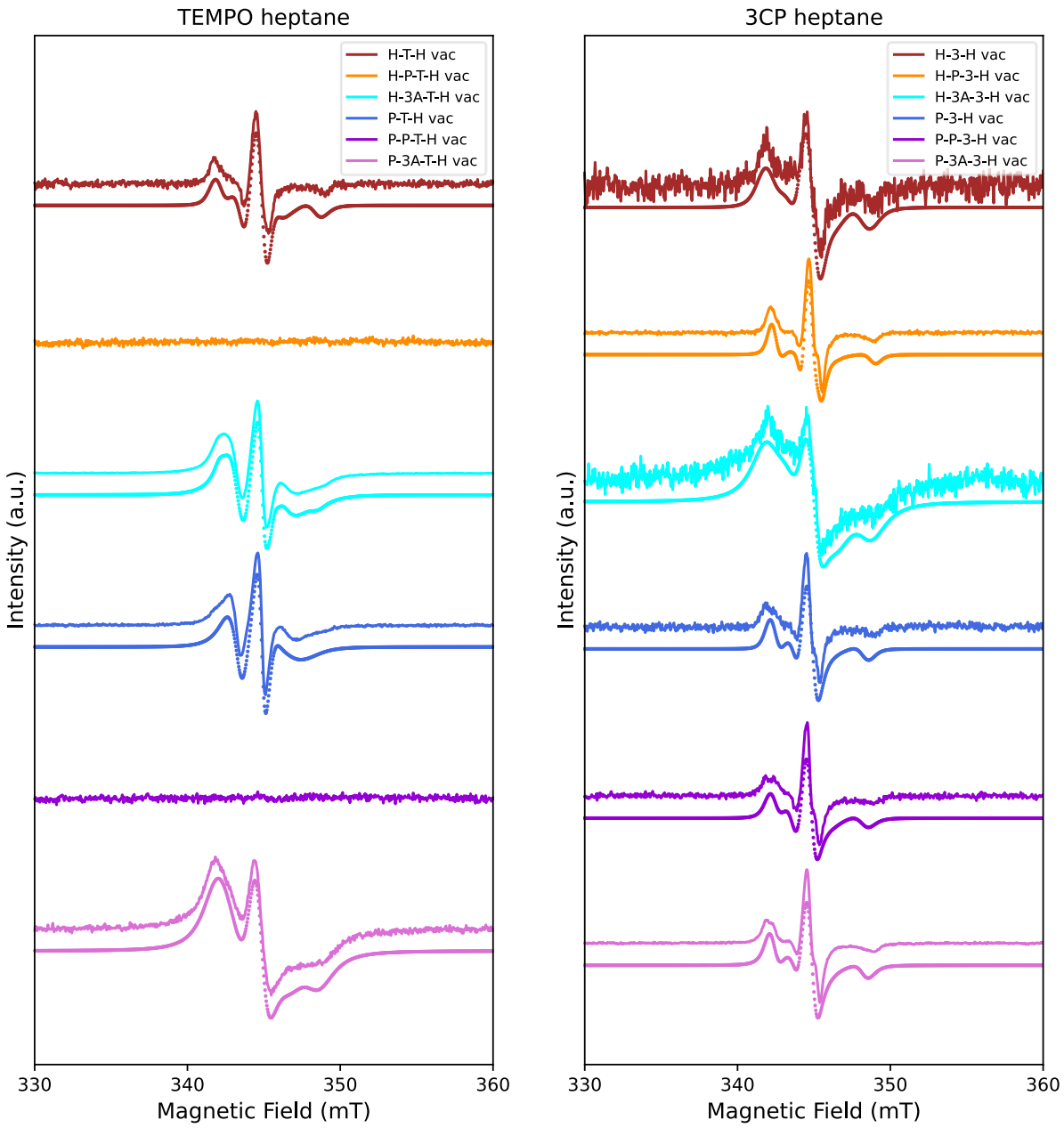


Figure S11. X-band cw-EPR spectra measured at room temperature under vacuum (marked as "vac") of TEMPO (left) and 3CP (right) adsorbed on unmodified, PPA- and 3APPA-modified TiO_2 Hombikat M311 and TiO_2 P25. Heptane was used as the solvent in the adsorption process. The simulated spectra are shown just below the respective experimental spectra. For sample labeling nomenclature: see section 2.2, main text.

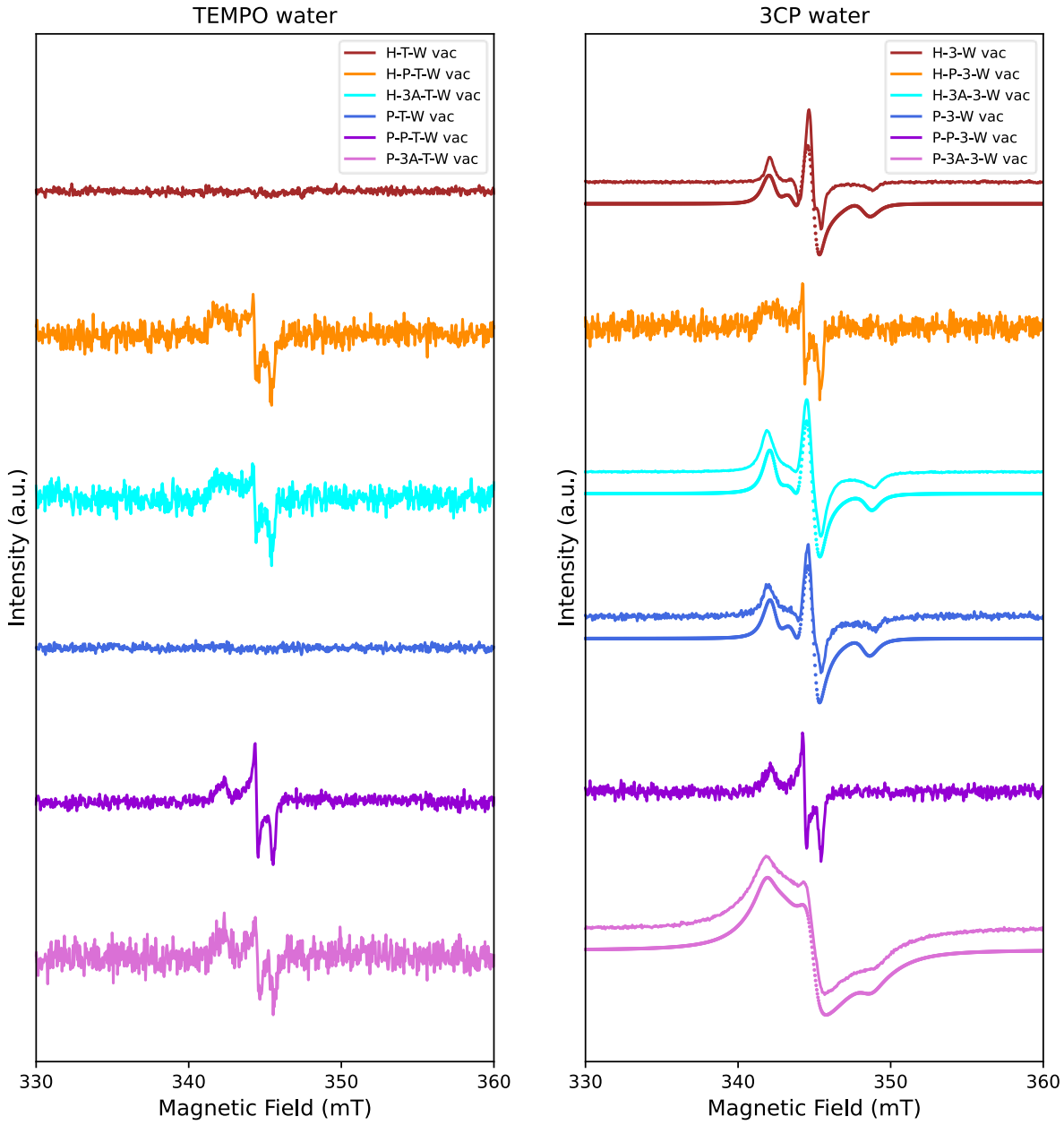


Figure S12. X-band cw-EPR spectra measured at room temperature under vacuum (marked as "vac") of unmodified, PPA- and 3APPA-modified TiO_2 Hombikat M311 and TiO_2 P25 samples adsorbed with TEMPO (left) and 3CP (right. Water was used as the solvent in the adsorption process. The simulated 3CP spectra are shown just below the respective experimental spectra. The spectra of H-P-T-W vac, H-3A-T-W vac, P-P-T-W vac, P-3A-T-W vac, H-P-3-W vac, and P-P-3-W vac exhibit signals of the Ti-O_2^- radical [2] and the simulations are not shown here. For sample labeling nomenclature: see section 2.2, main text.

Reference

1 K. Zhang, J. Wang and V. Meynen, Understanding surface (un)reactive sites of titania supports towards propyl-phosphonic acid surface modification, *Surfaces and Interfaces*, 2024, **44**, 103697.

2 N. Gys, B. Pawlak, K. Marcoen, G. Reekmans, L. F. Velasco, R. An, K. Wyns, K. Baert, K. Zhang, L. L. Lufungula, A. Piras, L. Siemons, B. Michielsen, S. Van Doorslaer, F. Blockhuys, T. Hauffman, P. Adriaensens, S. Mullens and V. Meynen, Self-Induced and Progressive Photo-Oxidation of Organophosphonic Acid Grafted Titanium Dioxide, *Chempluschem*, 2023, **88**, e202200441.

Collaborative research

S. Van Doorslaer, V. Meynen, H.Y.V. Ching, and R. An designed the research and analyzed and interpreted all data. R. An performed most of the synthesis of the modified samples, characterizations, adsorption of spin probes, and EPR measurements. A part of the adsorption of spin probes and EPR measurements was performed by L. Van der heyden. F. R. Tharakan and C. Chandran performed the methanol sorption and DRIFT measurements. Further interpretation of all data was accomplished through discussion between all authors.

Data sharing

Data will be made publically available upon publication at https://osf.io/9j8tk/