Electronic supplementary information

Synthesis and oxidation catalysis of a Ti-substituted phosphotungstate, and identification of the active oxygen species

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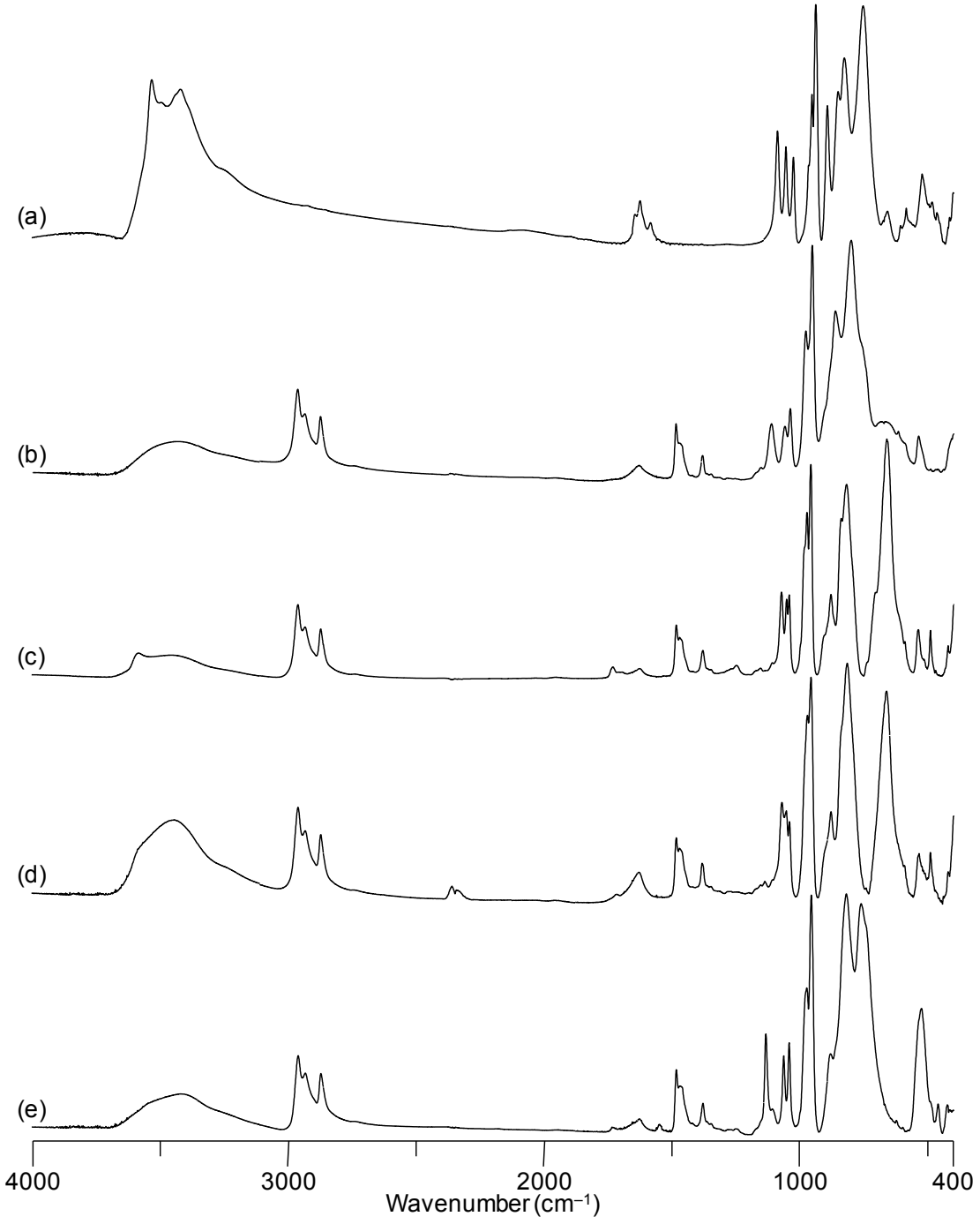


Fig. S1 IR spectra of (a) $Cs_7[\gamma\text{-}PW_{10}O_{36}]$, (b) PW10, (c) **I**, (d) **I** after the fifth reuse experiment, and (e) **II**.

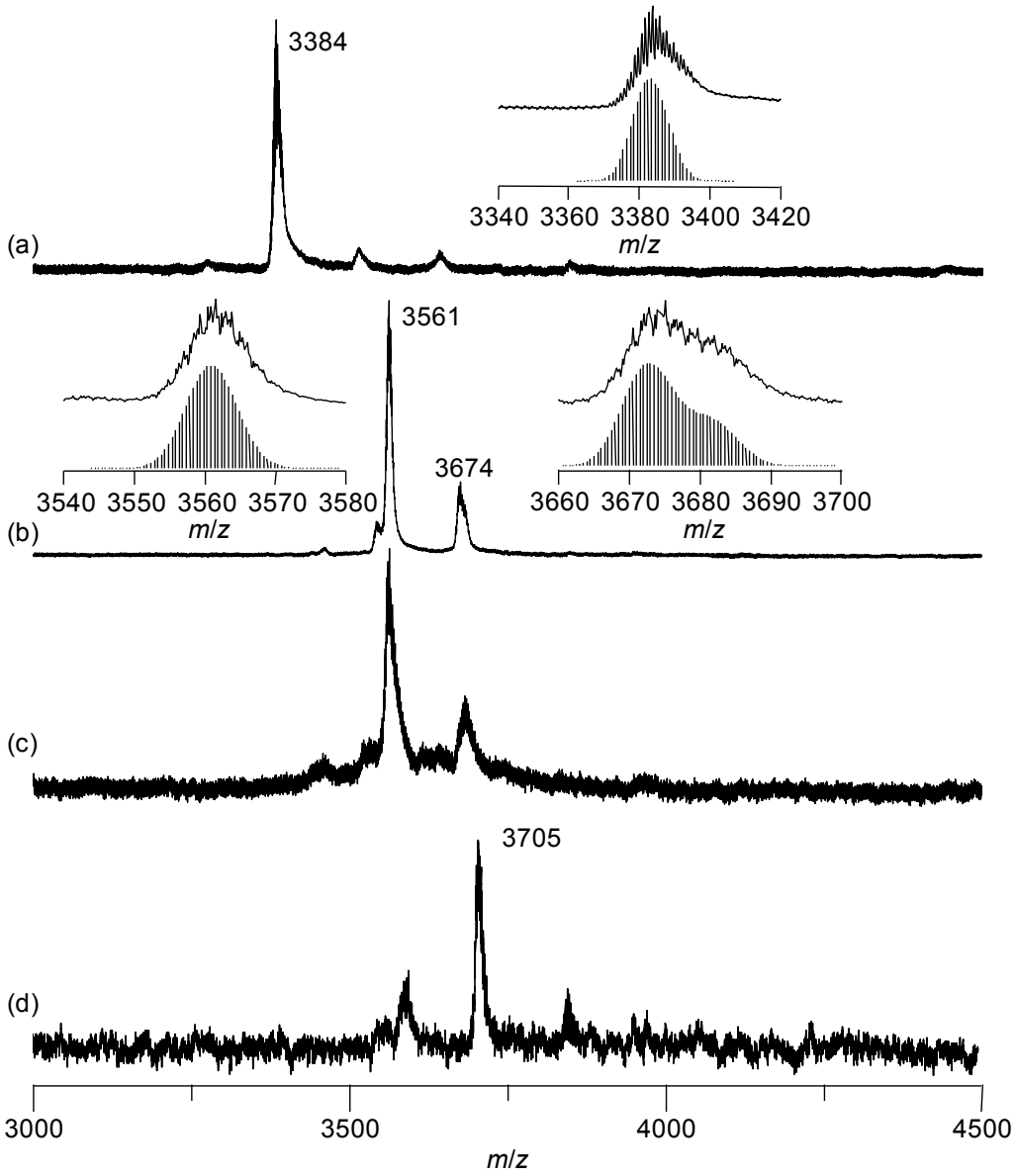


Fig. S2 CSI-MS spectra of (a) PW10 in acetone, (b) **I** in CH_3CN, (c) **I** after the fifth reuse experiment in CH_3CN, (d) isolated single crystals of **II** in CH_3CN. Insets: (a) spectrum in the range of 3340–3420 and simulated pattern for $[TBA_4(PW_{10}O_{34})]^+$ (*m*/*z* 3384); (b) spectra in the range of 3540–3580 and 3660–3700 and simulated patterns for $[TBA_8H_4\{(PW_{10}O_{36})_2Ti_4O_6\}]^{2+}$ (*m*/*z* 3561), $[TBA_9H\{(PW_{10}O_{36})_2Ti_4O_5\}]^{2+}$ (*m*/*z* 3673), and $[TBA_9H_3\{(PW_{10}O_{36})_2Ti_4O_6\}]^{2+}$ (*m*/*z* 3682).

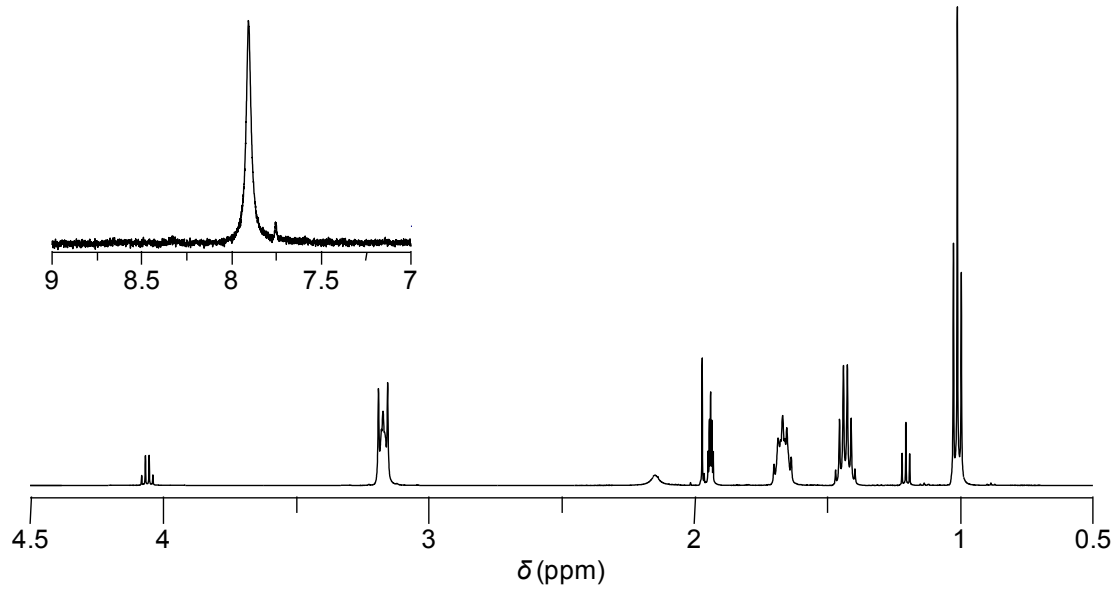


Fig. S3 ^{1}H NMR spectrum of **I** in CD_3CN.

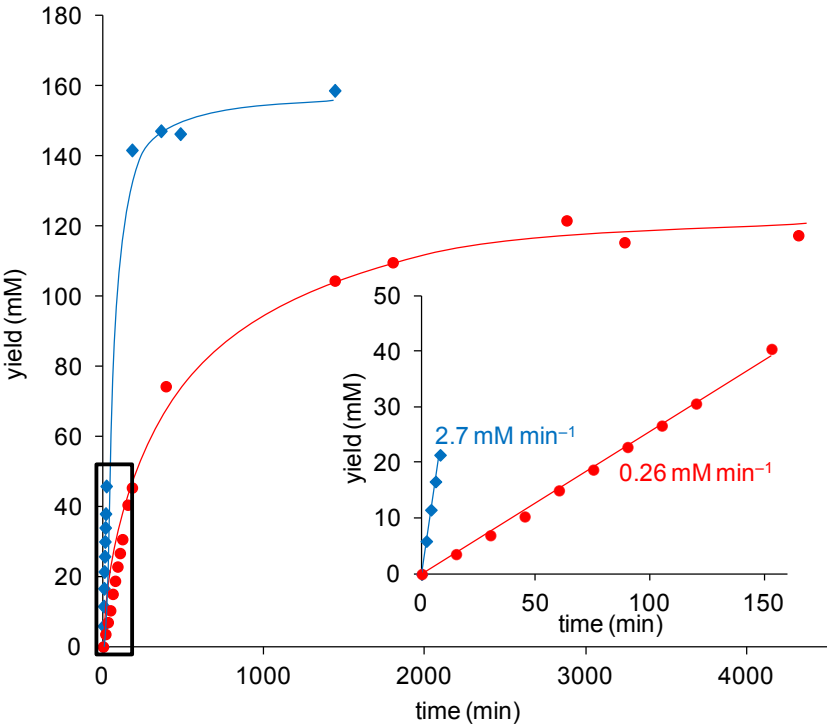


Fig. S4 Reaction profiles for the epoxidation of cyclooctene with H_2O_2 catalyzed by **I** (◆) and $TBA_8[(\gamma\text{-}SiW_{10}O_{36})_2Ti_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (●). Reaction conditions: Catalyst (1 μmol), cyclooctene (5 mmol), 30% H_2O_2 (1 mmol), CH_3CN (6 mL), 305 K.

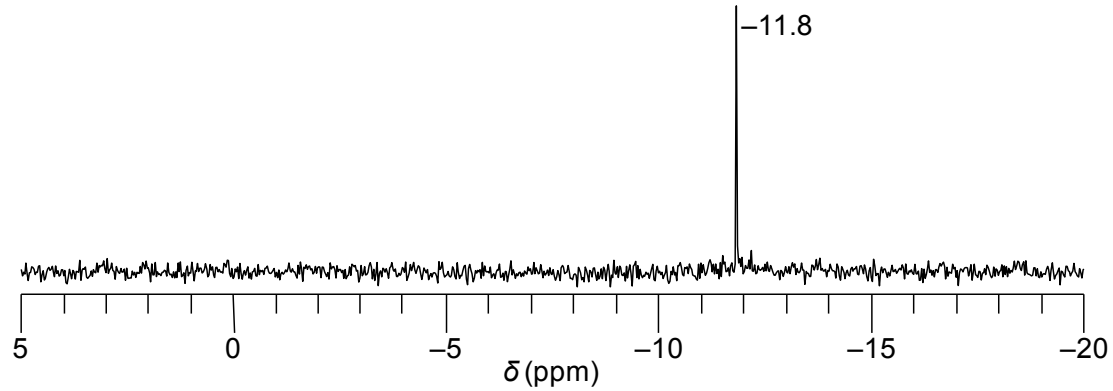


Fig. S5 ^{31}P NMR spectrum of **I** after the fifth reuse in CD_3CN.

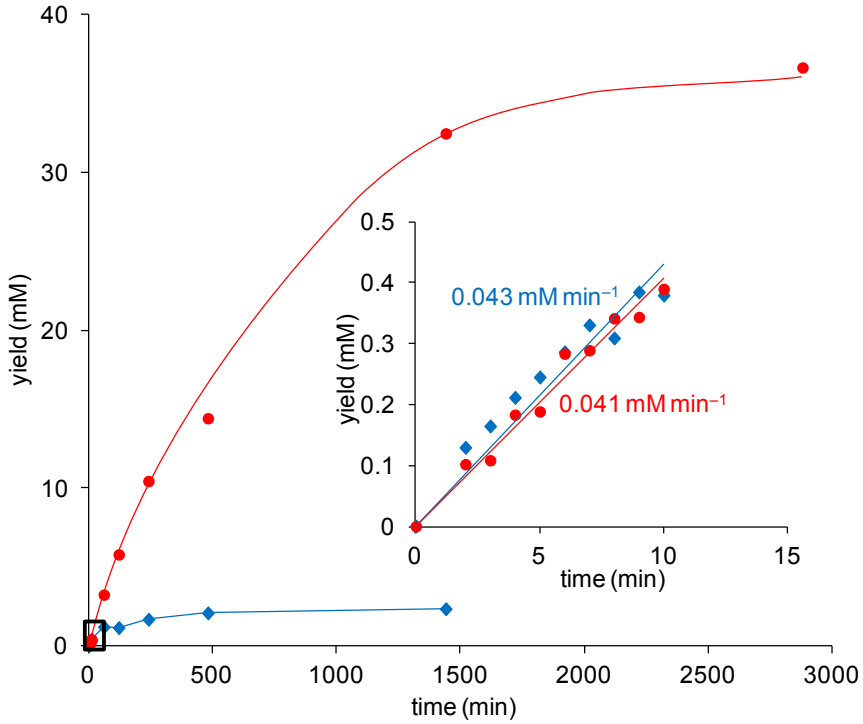
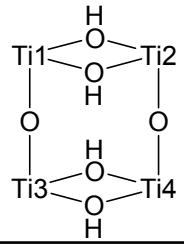


Fig. S6 Reaction profiles for the "stoichiometric" epoxidation of cyclooctene with **II** (◆) and the "catalytic" epoxidation of cyclooctene with H_2O_2 catalyzed by **I** (●). Reaction conditions for the stoichiometric epoxidation: **II** (0.57 mM), cyclooctene (0.035 M), CH_3CN, 253 K. Reaction conditions for the catalytic epoxidation: **I** (0.57 mM), cyclooctene (0.035 M), 90% H_2O_2 (0.14 M), CH_3CN, 253 K. Depending on the reaction conditions, the volume of CH_3CN was changed to keep a total volume of cyclooctene, 90% H_2O_2, and CH_3CN constant (7 mL). Under the present conditions, the epoxidation hardly proceeded in the absence of **I**.

Table S1 Crystallographic Data for **I** and **II**

	I	**II**
formula	$C_{104}N_6O_{82}P_2Ti_4W_{20}$	$O_{80}P_2Ti_4W_{20}$
fw	6575.64	5210.54
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	P-1 (No.2)
a (Å)	23.1112(1)	20.570(4)
b (Å)	15.2701(1)	34.716(7)
c (Å)	27.7104(2)	54.711(11)
α (deg)	90.0000	88.88(3)
β (deg)	108.7383(4)	85.12(3)
γ (deg)	90.0000	79.80(3)
V (Å^3)	9260.96(10)	38312(13)
Z	2	8
μ (mm^{-1})	12.617	25.366
R_1 ($I > 2\sigma(I)$)	0.0381	0.0999
wR_2	0.1076	0.2470

Table S2 Selected Bond Lengths and Angles in Ti-Substituted POMs $[(\gamma\text{-}XW_{10}O_{36})_2Ti_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]^{n-}$ (X = P, Si, or Ge)



X	Ti1···Ti2 Ti3···Ti4 (Å)	Ti1···Ti3 Ti2···Ti4 (Å)	Ti–OH (Å)	Ti–O (Å)	Ti···X (Å)	Ti–OH–Ti (deg)	Ti–O–Ti (deg)	ref.
P (**I**)	3.18	3.48	1.98–2.00	1.79–1.80	3.77–3.79	105.58–106.58	151.09	this work
Si	3.14–3.15	3.50–3.52	1.96–2.07	1.77–1.82	3.61–3.69	100.74–106.28	157.61–159.63	4a
Ge	3.01	3.49	1.90–1.94	1.81	3.60–3.61	101.87–104.12	149.46	23

Table S3 Epoxidation of Cyclooctene with H_2O_2 Catalyzed by Ti-Substituted POMs

entry	Ti-POM	catalyst (mM)	sub. (M)	H_2O_2 (M)	temp. (K)	solvent	time (h)	conv. (%)	yield (%)	ref.
1	**I**	0.60	0.75	0.15	305	CH_3CN	1	—	97	this work
2	**I**	0.60	0.15	0.15	305	CH_3CN	3.5	—	94	this work
3	$TBA_8[(\gamma\text{-}SiW_{10}O_{36})_2Ti_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$	0.60	0.75	0.15	323	CH_3CN	3	—	98	4a
4	$TBA_8[(\gamma\text{-}SiW_{10}O_{36})_2Ti_4(\mu\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}OMe)_2]$	0.60	0.75	0.15	323	CH_3CN	3	—	26	4a
5	$TBA_4H_2[\alpha\text{-}SiW_{11}TiO_{40}]$	0.60	0.75	0.15	323	CH_3CN	3	—	3	4a
6	$(4\text{-ddp})_{1.5}Na_{5.5}[PW_{10}Ti_2O_{40}]\cdot 5H_2O$[a]	0.63	0.19	0.38	342	CH_3CN	10	80	70	4b
7	$(4\text{-dea})_3Na_4[PW_{10}Ti_2O_{40}]\cdot 9H_2O$[b]	0.63	0.19	0.38	342	CH_3CN	10	43	38	4b
8	$TBA_5[PW_{11}TiO_{40}]$	0.63	0.19	0.38	323	CH_3CN/CH_2Cl_2	10	58	54	4b
9	$(4\text{-ddp})_{4.5}Li_{0.5}[PW_{11}TiO_{40}]\cdot 14H_2O$	0.63	0.19	0.38	323	CH_3CN/CH_2Cl_2	10	31	26	4b
10	$(4\text{-dea})_{4.5}Li_{0.5}[PW_{11}TiO_{40}]\cdot 4H_2O$	0.63	0.19	0.38	323	CH_3CN/CH_2Cl_2	10	30	21	4b
11	$TBA_5K_2[PW_{10}Ti_2O_{40}]\cdot 6H_2O$	0.63	0.19	0.38	323	CH_3CN/CH_2Cl_2	10	59	56	4b
12	$(4\text{-ddp})_4(i\text{-}PrNH_3)H_2[PW_{10}\{Ti(O_2)\}_2O_{38}]\cdot H_2O$	0.63	0.19	0.38	323	CH_3CN/CH_2Cl_2	10	94	—	4b
13	$(4\text{-ddp})_4(i\text{-}Pr_2NH_2)[PW_{11}\{Ti(O_2)\}O_{39}]\cdot H_2O$	0.31	0.19	0.38	323	CH_3CN/CH_2Cl_2	10	~58	—	4b
14	$(C_{12}mim)_5[PW_{11}TiO_{40}]$[c]	7.1	0.73	0.36	333	CH_3CN	6	~75	—	4c
15	$(C_{12}mim)_5[PW_{11}TiO_{40}]$	7.1	0.73	0.36	333	EtOAc	4	>99	—	4c
16	$(CTA)_5[PW_{11}TiO_{40}]$[d]	7.1	0.73	0.36	323	EtOAc	6	~80	—	4c
17	$TBA_{4.5}K_{0.5}[(\alpha\text{-}PW_{11}O_{39})\{Ti(OH_2)(ox)\}_2(\mu\text{-}O)]$[e]	0.63	0.24	0.30	298	CH_3CN/CH_2Cl_2	1	24.3	—	4e
18	$TBA_7[(PW_{11}TiO_{39})_2(\mu\text{-}OH)]$	0.63	0.24	0.30	298	CH_3CN/CH_2Cl_2	1	0.439	—	4e
19	$TBA_7KH_2[(\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{38})_2(\mu\text{-}O)_2]$	0.63	0.24	0.30	298	CH_3CN/CH_2Cl_2	1	1.22	—	4e
20	$TBA_7KH_4[(\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{37})_2(\mu\text{-}O)_3]$	0.63	0.24	0.30	298	CH_3CN/CH_2Cl_2	1	3.37	—	4e
21	$TBA_4(i\text{-}Pr_2NH_2)_2H[\alpha\text{-}PW_{10}\{Ti(O_2)\}_2O_{38}]\cdot 2H_2O$	0.67	0.2	0.933	342	CH_3CN	24	99.5	94.5	4f
22	$TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}[(B\text{-}\alpha\text{-}AsW_9O_{33})_2\{Ti(OH)\}_2\{WO(H_2O)\}]$	2	0.1	0.1	323	CH_3CN	5	70	66.5	4g

[a]ddp = diazodiphenylamine. [b]dea = diazodiethylaniline. [c]C_{12}mim = 1-dodecyl-3-methylimidazolium. [d]CTA = cetyltrimethylammonium. [e]ox = oxalate.