Supporting Information

Thermal stability of mesoscopic compounds of cetyltrimethylammonium and Keggin meta-tungstates

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Figure S1(a): Powder XRD pattern (Cu K α) of [CTA]_(y-x)[H_xWO₃(OH)_y], the product retrieved after 1 day of WCl₆ hydrolysis in the presence of CTA⁺. Stick plots are from JC-PDF 00-018-1420 and 01-084-0886 for H₂WO₄.H₂O (-), and WO₃.2H₂O (-) respectively. The lamellar-separation peak appears at 3.519° (d = 25.1 Å).



Figure S1(b): Raman spectrum of $[CTA]_{(y-x)}[H_xWO_3(OH)_y]$ collected with 633 nm excitation. $v(N-R_4^+)$, $v(-CH_3)$, $v(-CH_2-)$, $v(CH_3 \cdot \cdot N^+)$, $\delta(-CH_3)$ and $\sigma(N-R_4^+)$ vibrations appear at 3595, 2969, 2925–2845, 2721, 1447 and 1294 cm⁻¹ respectively, belonging to aliphatic CTA⁺. Three non-equivalent v(W=O) vibrations, from three POM species and/or W=O bond lengths,¹ appear at 999, 979 and 956 cm⁻¹. The double-peak with a maximum at 657 cm⁻¹ and the peaks at 375 and 264 cm⁻¹ are assigned to v(-O-W-O-), $v(-W-OH_2)$ and v(-W-O-W-) vibrations respectively. Raman-active lattice-modes of surfactant-tungstate hybrids appear from 194–120 cm⁻¹.²



Figure S1(c): FT-IR Spectrum of $[CTA]_{(y-x)}[H_xWO_3(OH)_y]$ (KBr pellet). Broad peaks from 3512 to 3161 cm⁻¹ are assigned to non-equivalent v(-OH) species. Peaks at 3039, 2920 and 2848 cm⁻¹ arise from $v(-N^+(CH_3))$, $v_{as}(-CH_2-)$ and $v_{ss}(-CH_2-)$ vibrations of CTA⁺, respectively.³ The broad peak centered on 1616 cm⁻¹ is assigned to intercalated $\delta(H_2O)$. The asymmetric double-peak with a maximum at 1468 cm⁻¹ corresponds to $\omega(-CH_2-)$, $\delta(-CH_2-)$ and $\sigma(-CH_3)$ modes. The small peak at 1005 cm⁻¹ is from the v(-N-C-) vibration.^{2, 4} Peaks at 958 and 893 cm⁻¹ correspond to v(W=O) and v(-O-W-O-) vibrations from the WO4²⁻ anion, and the broad peak from 798 to 613 cm⁻¹ is due to $v(-O-W_c-O-)$ vibrations that arise from the polymerized sheets of WO4^{2-.5}



Figure S2(a): Powder XRD pattern of the product of WCl₆ hydrolysis after the course of one day in de-ionized H₂O (WO₃/H₂WO₄.*x*H₂O). Stick plots are generated from the same JC-PDFs seen in Figure S2(a).



Figure S2(b): Raman spectrum of WO₃/H₂WO₄.*x*H₂O. The small peak at 946 cm⁻¹ is due to the v(W=O) vibration from the WO₄²⁻ anion. Peaks at 806 and 705 cm⁻¹ correspond to non-equivalent v(-O-W-O-) stretching. The asymmetric peak with a maximum at 265 cm⁻¹ is comprised of δ (-O-W-O-) and v(-W-O-W-) modes, and bulk trioxide lattice modes are seen at 187 and 132 cm⁻¹.²



Figure S2(c): FT-IR spectrum of WO₃/H₂WO₄.*x*H₂O collected on a KBr pellet. The broad peak from 3523 to 3150 cm⁻¹ and extending towards the lower-energy region is assigned to differing v(-OH) groups arising from absorbed water. The broad peak centered on 1616 cm⁻¹ is assigned to $\delta(\text{H}_2\text{O})$ vibrations of this water. The 916 cm⁻¹ peak is likely due to surface-terminating v(W=O), and the broad peak centered on 638 cm⁻¹ arises from v(-O-W-O-) vibrations throughout the bulk-lattice.⁶



Figure S3(a): Powder XRD pattern of the dried precipitate resulting from CTA^+ addition to a suspension of WO₃/H₂WO₄.*x*H₂O (produced by WCl₆ hydrolysis in H₂O for 1 day), then pH was raised to pH4 (-) and pH6 (-) and stirred for 1 week in an effort to promote metatungstate formation. The lamellar-separation peak, appears at 3.159°, in the same position as for $[CTA]_{(y-x)}[H_xWO_3(OH)_y]$ seen in Fig. S2(a). The H₂WO₄.H₂O stick-plot is made from the same JC-PDF as in Fig. S2(a).



Figure S3(b): Raman spectra of the dried precipitate resulting from CTA⁺ addition to a suspension of WO₃/H₂WO₄.*x*H₂O (produced by WCl₆ hydrolysis in H₂O for 1 day), then pH was raised to pH4 (-) and pH6 (-) and stirred for one week in an effort to promote metatungstate formation. $v(N-R_4^+)$, $v(-CH_3)$, $v(-CH_2-)$, $v(CH_3 \cdot \cdot N^+)$, $\delta(-CH_3)$ and $\sigma(N-R_4^+)$ vibrations appear at 3039, 2964, 2929–2850, 2726, 1445 and 1296 cm⁻¹ respectively, belonging to aliphatic CTA⁺. Three non-equivalent v(W=O) vibrations, from three POM species and/or W=O bond lengths,¹ appear at 1002, 967 and 958 cm⁻¹. The double-peak with a maximum at 634 cm⁻¹ and the peaks at 380 and 234 cm⁻¹ are assigned to v(-O-W-O-), $v(-W-OH_2)$ and v(-W-O-W-) vibrations respectively. Raman-active lattice-modes of surfactant-tungstate hybrids appear from 180–120 cm⁻¹.²



Figure S3(c): FT-IR spectra of the dried precipitate resulting from CTA⁺ addition to a suspension of WO₃/H₂WO₄.*x*H₂O (produced by WCl₆ hydrolysis in H₂O for 1 day), then pH was raised to pH4 (-) and pH6 (-) and stirred for 1 week in an effort to promote metatungstate formation. Broad peaks at 3514, 3355 and 3138 cm⁻¹ are due to non-equivalent *v*(-OH) species. Peaks at 3035, 2920 and 2851 cm⁻¹ arise from *v*(-N⁺(CH₃)), *v*_{as}(-CH₂) and *v*_{ss}(-CH₂-) vibrations of CTA⁺, respectively. The broad peak centered on 1590 cm⁻¹ is assigned to intercalated δ (H₂O). The asymmetric peak with a maximum at 1467 cm⁻¹ contains to δ (-CH₂-) and σ (-CH₂-) modes. The small peak at 1003 cm⁻¹ is from to the *v*(-N-C-) vibration.^{3,4} Peaks at 956 and 886 cm⁻¹ correspond to *v*(W=O) and *v*(-O-W_b-O-) vibrations. The relatively small size and asymmetry of these peaks is most likely due to poorly formed POMs, resulting from slow oxoanion equilibria kinetics⁷ (both of these solutions have been raised from pH 0.5 and aged for one week). The peak from 792 to 582 cm⁻¹ is due to *v*(-O-W_c-O-) vibrations.⁸



Figure S4(a): Powder XRD pattern of the precipitate collected from a CTA-tungstate solution where WCl₆ was hydrolyzed in H₂O for 1 day, followed by NH₄OH addition the next day to a pH of 4, CTA-Br was then added the next day before filtration 2 hrs later. The lamellar-separation peak appears at 2.079° (d=42.5 Å) and the pseudo-hexagonal order of the POMs is manifested at 9.48° (d = 9.33 Å) as a broad, asymmetric peak. This broadness and asymmetry of the 9.48° peak, as well as those centered on 30 and 55° is due to the wide array of POM species produced during the product's synthesis (when pH was adjusted),⁷ which results in a largely amorphous hydrophilic region.



Figure S4(b): Raman spectrum of the product described within Figure S5(a). $v(N-R_4^+)$, $v(-CH_3)$, $v(-CH_2-)$, $v(CH_3 \cdot N^+)$, $\delta(-CH_3)$ and $\sigma(N-R_4^+)$ vibrations appear at 3035, 2967, 2924–2851, 2724, 1446 and 1302 cm⁻¹ respectively, belonging to aliphatic CTA⁺. Three non-equivalent v(W=O) vibrations, from three POM species and/or W=O bond lengths,¹ appear at 989, 983 and 963 cm⁻¹. The width and asymmetry of the peak at 963 cm⁻¹ is indicative of differing POM species.⁹ The broad peak with a maximum at 655 cm⁻¹ and the peaks at 431 and 233 cm⁻¹ are assigned to v(-O-W-O), $v(-W-OH_2)$ and v(-W-O-W-) vibrations respectively. Raman-active lattice-modes of surfactant-tungstate hybrids appear from 180–126 cm⁻¹.²



Figure S4(c): FT-IR spectrum of the product described within Figure S5(a). Broad peaks at 3430 and 3203 cm⁻¹ are assigned to non-equivalent v(-OH) species. Peaks at 3033, 2921 and 2851 cm⁻¹ arise from $v(\text{-N}^+(\text{CH}_3))$, $v_{as}(\text{-CH}_2)$ and $v_{ss}(\text{-CH}_2)$ vibrations of CTA⁺, respectively. The broad peak centered on 1618 cm⁻¹ is assigned to intercalated $\delta(\text{H}_2\text{O})$. The asymmetric peak with a maximum at 1465 cm⁻¹ contains $\omega(\text{-CH}_2\text{-})$, $\delta(\text{-CH}_2\text{-})$ and $\sigma(\text{-CH}_2\text{-})$ modes. Peaks at 958 and 886 cm⁻¹ correspond to v(W=O) and $v(\text{-O-W}_b\text{-O-})$ vibrations. The relatively small size and asymmetry of these peaks is most likely due to poorly formed POMs, resultant from slow oxoanion equilibria kinetics as solution pH is changed.⁷ The broad, asymmetric peaks at 796 and 585 cm⁻¹ are due to $v(\text{-O-W}_c\text{-O-})$ vibrations that arise from the polymerized, differing, oxoanions.⁸



Figure S5(a): Powder XRD pattern of a CTA-tungstate solution (prepared in the same way as depicted in Figure S2(a)) which was then raised to pH 8 with NH₄OH and stirred overnight before HCl was used to acidify to pH 7 (-) and pH 4 (-). The lamellar-separation peak appears at 2.120° (d=41.7 Å, very close to the 44 Å of two CTA+ entities placed end-to-end)) and the pseudo-hexagonal order of the POMs is manifested at 9.076° (d = 9.74 Å) as a broad, asymmetric peak. This broadness and asymmetry of the 9.076° peak, as well as those centered on about 30 and 60° is due to the wide array of POM species produced during the products synthesis (when pH was adjusted),⁷ which results in a largely amorphous hydrophilic region. The pattern is very similar to that displayed in Figure S5(a), and most likely due to the mutual inclusion of differing POMs.



Figure S5(b): Raman spectra of the product described in Figure S6(a). $v(N-R_4^+)$, $v(-CH_3)$, $v(-CH_2-)$, $v(CH_3 \cdot N^+)$, $\delta(-CH_3)$ and $\sigma(N-R_4^+)$ vibrations appear at 3034, 2967, 2963–2849, 2731, 1448 and 1301 cm⁻¹ respectively, belonging to aliphatic CTA⁺. A large, asymmetric double-peak attributable to v(W=O) vibrations, (due to differing POM species and/or W=O bond lengths,¹) appear at 1002 and 982 cm⁻¹. The width and asymmetry of the peak at 982 cm⁻¹ is indicative of differing POM species.⁹ The peak at 233 cm⁻¹ is assigned to v(-W-O-W-). Raman-active lattice-modes of surfactant-tungstate hybrids appear from 180–127 cm⁻¹.²



Figure S5(c): FT-IR spectrum of the product described within Figure S6(**a**). Broad peaks at 3449 and 3200 cm⁻¹ are assigned to non-equivalent *v*(-OH) species. Peaks at 3041, 2921 and 2850 cm⁻¹ arise from *v*(-N⁺(CH₃)), *v*_{as}(-CH₂) and *v*_{ss}(-CH₂-) vibrations of CTA⁺, respectively. The broad peak at 1623 cm⁻¹ is assigned to intercalated δ (H₂O). The asymmetric peak with a maximum at 1465 cm⁻¹ contains ω (-CH₂-), δ (-CH₂-) and σ (-CH₂-) modes. Peaks at 956 and 887 cm⁻¹ correspond to *v*(W=O) and *v*(-O-W_b-O-) vibrations. The relatively small size and asymmetry of these peaks is most likely due to poorly formed POMs, resulting from slow oxoanion equilibria kinetics as solution pH is changed.⁷ The broad peaks at 787, 669 and 584 cm⁻¹ are due to *v*(-O-W_c-O-) vibrations that arise from the polymerized, differing, oxoanions.⁸



Site	Keggin 1934 ¹⁰	Asami <i>et al.</i> 1984 ¹¹	Rocchiccioli- Deltcheff <i>et al.</i> 1976 ¹² , Nomiya & Miwa 1984 ¹³
1	O ₁	O _i ('internal'_	O _a
2	O ₂	O _c ('corner)	Ob
3	O ₃	O _e ('edge')	Oc
4	O_4	Ot ('terminal')	Od

Figure S6: Structure of Keggin ion H₂W₁₂O₄₀⁶⁻ (internal hydrogens not shown). There are four types of oxygen sites. Here we use the notation of Rocchiccioli-Deltcheff *et al.*¹² to differentiate them as O_a, O_b, O_c and O_d. The relationship of these site labels to those given by Keggin in 1934 and those allocated by Asami *et al.* in 1984 are shown above as well.



Figure S7: Raman spectrum of CTA-W₁₂ at room-temperature. $v(-N^+(CH_3))$, $v(-CH_3)$, $v_{as}(-CH_2-)$, $v_{ss}(-CH_2-)$, $v(CH_3 \cdot \cdot N^+)$, $\delta(-CH_3)$ and $\sigma(N-R_4^+)$ vibrations appear at 3032, 2965, 2937–2847, 2732, 1447 and 1296 cm⁻¹ respectively, belonging to aliphatic CTA⁺. $v_{ss}(W=O)$ and $v_{as}(W=O)vibrations$ appear at 982 and 960 cm⁻¹.^{1, 5} The broad peak with a maximum at 582 cm⁻¹ and peaks at 342 and 229 cm⁻¹ correspond to v(-O-W-O-), $\delta(-W-OH_2)$ and v(-W-O-W-) vibrations respectively. Raman-active lattice-modes of surfactant-tungstate hybrids appear at 197 and 156 cm⁻¹.²



Figure S8: XPS spectra of CTA- W_{12} highlighting W4F(a), O1S(b), C1S(c) and N1S(d) regions. A small amount of W^{5+} can be seen in the W4F spectrum (a) due to oxygen-vacancies created during the measurement within the very high-vacuum environment. (-W-O-) and (-W-OH) can be seen within (b), corresponding to the Keggin cage and a small amount of absorbed moisture, respectively. (-C-C/-C-H) and (-C-N-) species can be seen in (c) corresponding to the alkyl-chain and head-group of CTA⁺, respectively. The sole environment of N can be seen in (d), depicting the cationic-nitrogen within the CTA⁺ head-group.







W	/4	L-selles	40.75	47.1	0.00	1.49
С	6	K-series	29.09	29.32	57.9	5.11
0	8	K-series	17.54	17.68	26.21	3.29
N	7	K-series	5.68	5.73	9.7	1.84
Cl	17	K-series	0.16	0.17	0.11	0.04
		TOTAL:	99.2	100	100	

Figure S9: EDX analysis of CTA-W12. a) secondary-electron image of analyzed area. b) Elemental map of elements analyzed. c) Carbon Kα map. d) Nitrogen Kα map. e) Oxygen Kα map. f) Chlorine Kα map. g) Tungsten Kα map. h) EDX spectrum. TABLE: Quantification of EDX result, weight and atomic % are skewed due to inability to analyze for hydrogen.



Figure S10: Thermogravimetric analysis of thermal decomposition of pure CTA-Br. Two endotherms can be seen at 38 and 110°C. These are without any associated mass loss and are likely due to thermally instigated reorganization of the alkyl-chains. Mass loss begins at 190°C which coincides initially with an exothermic event. This process then becomes endothermic at ~250°C as the CTA-Br cracks and vaporizes in the crucible before, finally, becoming exothermic again at 300°C. At this temperature combustion of the most of the remaining organic (about 9% of the starting mass) occurs. Finally, at around 440°C, the remaining carbon in the sample is combusted.



Figure S11. Measured X-ray pattern of phase V compared to patterns produced from two simplified structural models. Data shown is for ~270 °C.

References

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