Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information

Chain length effects on the size, stability, and electronic structure of redox-active organic-inorganic hybrid polyoxometalate micelles

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Contents

Methods

^{1}H NMR- and ^{31}P NMR-spectra were obtained using either Bruker DPX 400 MHz or Bruker 500 MHz spectrometers.

Electrospray ionisation mass spectrometry (ESI-MS) was performed on a Bruker MicroTOF spectrometer operating in negative mode. Samples were prepared for analysis by dissolving ca. 1 mg of the solid compound in 1 mL of HPLC grade acetonitrile. 50 μL of this stock solution was then introduced to the spectrometer through an auto-sampler by mixing into a stream of 30:70 H_2O:MeOH. All data was subsequently analysed using the Bruker DataAnalysis software suite.

In all cases, operating parameters for the spectrometer were as follows: capillary voltage: 5 kV; end plate off-set voltage: 500 V; dry gas flow rate: 4 L min-1; dry (source) temperature: 200 °C.

Dynamic Light Scattering (DLS) and Zeta-potential measurements were acquired using a Malvern Instrument Nano-ZS Zetasizer. All measurements were performed at room temperature.

CHN microanalysis was carried out using a CE-440 Elemental Analyser by Exeter Analytical (with thanks to the analytical services in the School of Chemistry, University of Nottingham).

Electrochemical measurements were performed on a CH Instruments CHI600e workstation. Full details of electrochemical methods and experimental set-up are reported in the corresponding section below.

TEM imaging was performed using a JEOL 2100F FEG transmission field electron microscope (field emission gun source, information limit 0.19 nm) operating at an accelerating voltage of 200 kV. TEM samples were prepared by drop-casting several drops of sample onto copper-mesh TEM grid mounted with a lacey carbon support and graphene oxide film. Samples were dried under high vacuum unless stated otherwise.

Thermal gravimetric analysis was conducted at a heating rate of 10°C min^{-1} under air.

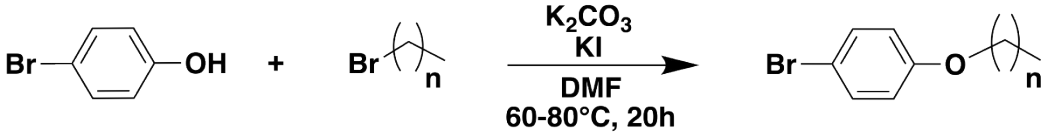
Infra-red spectra were measured using a Bruker Alpha FTIR spectrometer with a platinum ATR module.

All microwave syntheses were carried out in a CEM discover microwave reactor.

Synthesis

All reagents were obtained from commercial sources and were used without further purification. The precursors $K_6[P_2W_{18}O_{62}]$ and $K_{10}[P_2W_{17}O_{61}]$ were prepared by reported methods.[1]

Step 1 – Alkylation



***n*+1= 10 (*A*), 12 (*B*), 14 (*C*), 16 (*D*), 18 (*E*) and 20 (*F*)**

The general method for the preparation of each alkylated bromophenol intermediate is as follows: The corresponding bromoalkene compound (8.54 mmol) and 4-bromophenol (10.5 mmol) were dissolved in N,N-dimethylformamide (40 mL). To this solution, KI (1.51 mmol) and K_2CO_3 (32.6 mmol) were added, the reaction mixture was then heated (see below for exact temperatures) for 20h. The reaction was then cooled to room temperature and the solvent was removed *in vacuo*. The resulting solid product was dissolved in diethyl ether (100 ml) and washed with a combination of 2M NaOH (2 x 100 ml) and brine (100 ml). The organic fraction was dried over $MgSO_4$ and the solvent was removed in vacuo to yield an orange oil. The crude product was then recrystallized using a minimal amount of hot ethanol.

1-bromo-4-(decyloxy)benzene - $C_{16}H_{25}BrO$ **(1A)**

Colourless oil
Temperature = 60°C
Yield = 2.41 g (89 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.38 – 7.33 (m, 2H, C**H**), 6.80 – 6.74 (m, 2H, C**H**), 3.91 (t, J = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.81 – 1.71 (m, 2H, C$\mathbf{H_2}$), 1.49 – 1.39 (m, 2H, C$\mathbf{H_2}$), 1.38 –1.19 (m, 12H, C$\mathbf{H_2}$), 0.89 (t, J = 6.9 Hz, 3H, C$\mathbf{H_3}$).

1-bromo-4-(dodecyloxy)benzene - $C_{18}H_{29}BrO$ **(1B)**

White solid
Temperature = 70°C
Yield = 2.46 g (69 %).
^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.46 – 7.30 (m, 2H, C**H**), 6.88 – 6.63 (m, 2H, C**H**), 3.93 (t, *J* = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.79 (dt, *J* = 14.7, 6.7 Hz, 2H, C$\mathbf{H_2}$), 1.49 – 1.42 (m, 2H, C$\mathbf{H_2}$), 1.38 – 1.24 (m, 16H, C$\mathbf{H_2}$), 0.91 (t, *J* = 6.9 Hz, 3H, C$\mathbf{H_3}$).

1-bromo-4-(tetradecyloxy)benzene - $C_{20}H_{33}BrO$ **(1C)**

White solid
Temperature = 75°C
Yield = 2.86 g (95 %)
^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.38 (d, *J* = 8.7 Hz, 2H, C**H**), 6.80 (d, *J* = 8.7 Hz, 2H, C**H**), 3.94 (t, *J* = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.79 (p, *J* = 6.8 Hz, 2H, C$\mathbf{H_2}$), 1.46 (q, *J* = 7.7 Hz, 2H, C$\mathbf{H_2}$), 1.39 – 1.21 (m, 20H, C$\mathbf{H_2}$), 0.92 (t, *J* = 6.8 Hz, 3H, C$\mathbf{H_3}$).

[1] R. Contant, Inorganic Syntheses; John Wiley & Sons, 1990; Vol. 27, 107.

1-bromo-4-(hexadecyloxy)benzene - $C_{22}H_{37}BrO$ **(1D)**

White solid
Temperature = 75°C
Yield = 2.69 g (80 %)
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.45 – 7.32 (m, 2H, C**H**), 6.85 – 6.70 (m, 2H, C**H**), 3.93 (t, J = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.78 (dq, J = 8.2, 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.52 – 1.42 (m, 2H, C$\mathbf{H_2}$), 1.28 (s, 26H, C$\mathbf{H_2}$), 0.96 – 0.82 (m, 3H, C$\mathbf{H_3}$).

1-bromo-4-(octadecyloxy)benzene - $C_{24}H_{41}BrO$ **(1E)**

White solid
Temperature = 80°C
Yield = 3.07g (85 %)
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.43 – 7.32 (m, 2H, C**H**), 6.85 – 6.74 (m, 2H, C**H**), 3.93 (t, *J* = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.78 (dq, *J* = 8.1, 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.46 (dq, *J* = 11.7, 6.8 Hz, 2H, C$\mathbf{H_2}$), 1.28 (s, 28H, C$\mathbf{H_2}$), 0.97 – 0.85 (m, 3H, C$\mathbf{H_3}$).

1-bromo-4-(icosyloxy)benzene - $C_{26}H_{45}BrO$ **(1F)**

White solid
Temperature = 80°C
Yield = 3.05 g (78 %)
^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.44 – 7.33 (m, 2H, C**H**), 6.83 – 6.77 (m, 2H, C**H**), 3.93 (t, *J* = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.79 (dt, *J* = 14.8, 6.7 Hz, 2H, C$\mathbf{H_2}$), 1.52 – 1.41 (m, 2H, C$\mathbf{H_2}$), 1.28 (s, 32H, C$\mathbf{H_2}$), 0.91 (t, *J* = 6.9 Hz, 3H, C$\mathbf{H_3}$).

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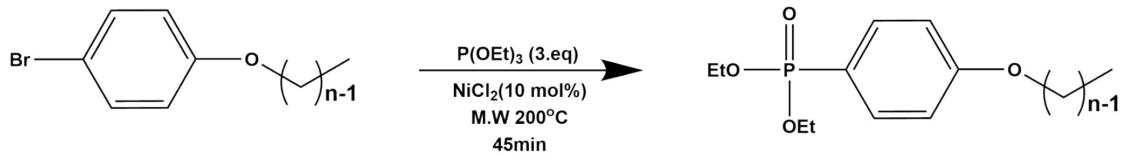
Step 2 – Phosphorylation



***n*+1= 10 (*A*), 12 (*B*), 14 (*C*), 16 (*D*), 18 (*E*) and 20 (*F*)**

The general method for phosphorylation of compound **1A-F** is as follows: To a microwave vessel, triethylphosphite (1.8 ml, 10.5 mmol) and anhydrous $NiCl_2$ (0.045 g, 0.35 mmol) was added, stirred and then purged with argon for 10 mins. Dried **1A-F** (3.5 mmol) was added to the black mixture, heated (until dissolved) and then purged with argon for a further 10 mins. The vessel was then heated under autogeneous pressure in the microwave reactor at 200 °C for 45 mins. The reaction mixture was then cooled to room temperature and dissolved in diethyl ether (100 ml). The resulting solution was then filtered and centrifuged for 15 mins at 8000 rpm. The black precipitate was filtered off and the solvent was evaporated *in vacuo* to give a yellow oil. The crude product was then dissolved in hot acetonitrile (60 mL) and filtered. Ethyl acetate (50 mL) was then added to the filtrate and the solvent was evaporated under vacuum.

diethyl-(4-(decyloxy)phenyl)phosphonate - $C_{20}H_{35}O_4P$ **(2A)**

Clear/Yellow oil
Yield = 0.67 g (57%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.66 (m, 2H, C**H**), 7.00 – 6.89 (m, 2H, C**H**), 4.20 – 3.96 (m, 6H, C$\mathbf{H_3}$), 1.81 (p, *J* = 6.7 Hz, 2H, C$\mathbf{H_2}$), 1.47 (p, *J* = 7.1 Hz, 2H, C$\mathbf{H_2}$), 1.39 – 1.18 (m, 18H, C$\mathbf{H_2}$/C$\mathbf{H_3}$), 0.95 – 0.71 (m, 3H, C$\mathbf{H_3}$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.89. ESI-MS (MeCN) *m/z* (calculated, found): $[L+H]^+$ (371.23, 371.23).

diethyl (4-(dodecyloxy)phenyl)phosphonate - $C_{22}H_{39}O_4P$ **(2B)**

Clear/Yellow oil
Yield = 0.95g (68%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 – 7.64 (m, 2H, C**H**), 7.06 – 6.87 (m, 2H, C**H**), 4.24 – 3.93 (m, 6H, C$\mathbf{H_2}$), 1.82 (q, *J* = 7.7, 7.2 Hz, 4H, C$\mathbf{H_2}$), 1.53 – 1.22 (m, 22H, C$\mathbf{H_2}$/C$\mathbf{H_3}$), 0.90 (t, *J* = 6.9 Hz, 3H, C$\mathbf{H_3}$).
^{31}P NMR (202 MHz, Chloroform-*d*) δ 19.90.
ESI-MS (MeCN) *m/z* (calculated, found): $[L\text{-}OEt]^-$(369.22,369.22)

diethyl (4-(tetradecyloxy)phenyl)phosphonate - $C_{24}H_{43}O_4P$ **(2C)**

Yellow oil
Yield = 0.97g (65%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 – 7.67 (m, 2H, C**H**), 7.02 – 6.92 (m, 2H, C**H**), 4.20 – 3.96 (m, 6H, C$\mathbf{H_2}$), 1.86 – 1.76 (m, 2H, C$\mathbf{H_2}$), 1.52 – 1.22 (m, 30H, C$\mathbf{H_2}$/C$\mathbf{H_3}$), 0.89 (t, *J* = 6.9 Hz, 3H, C$\mathbf{H_3}$).
^{31}P NMR (202 MHz, Chloroform-d) δ 19.89.
ESI-MS (MeCN) *m/z* (calculated, found): $[L+H]^+$ (427.3,427.3)

diethyl (4-(hexadecyloxy)phenyl)phosphonate- $C_{26}H_{47}O_4P$ **(2D)**

Yellow waxy solid
Yield = 1.02g (64%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 12.7, 8.4 Hz, 2H, C**H**), 6.96 (dd, *J* = 8.7, 3.4 Hz, 2H, C**H**), 4.18 – 4.00 (m, 4H, C$\mathbf{H_2}$), 4.00 (t, *J* = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.80 (p, *J* = 6.8 Hz, 2H, C$\mathbf{H_2}$), 1.51 – 1.41 (m, 2H, C$\mathbf{H_2}$), 1.32 (t, *J* = 7.0 Hz, 6H, C$\mathbf{H_2}$), 1.27 (s, 24H, C$\mathbf{H_2}$/C$\mathbf{H_3}$) , 0.89 (t, *J* = 6.8 Hz, 3H, C$\mathbf{H_3}$).^{31}P NMR (202 MHz, Chloroform-*d*) δ 19.90.
ESI-MS (MeCN) *m/z* (calculated, found): $[L+H]^+$ (455.33, 455.32).

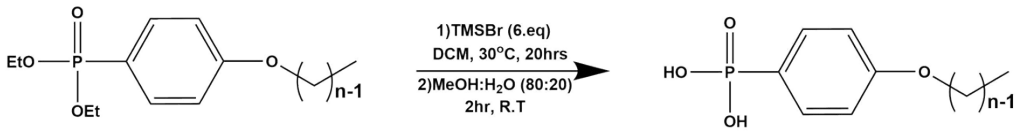
diethyl (4-(octadecyloxy)phenyl)phosphonate - $C_{28}H_{51}O_4P$ **(2E)**

Off-white waxy solid
Yield = 1.03g (61%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.63 (m, 2H, C**H**), 7.04 – 6.89 (m, 2H, C**H**), 4.29 – 3.92 (m, 6H, C$\mathbf{H_2}$), 1.81 (dt, *J* = 14.0, 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.53 – 1.42 (m, 2H, C$\mathbf{H_2}$), 1.40 – 1.17 (m, 34H, C$\mathbf{H_2}$/C$\mathbf{H_3}$), 0.90 (t, *J* = 6.9 Hz, 3H, C$\mathbf{H_3}$). ^{31}P NMR (202 MHz, $CDCl_3$) δ 19.7.
ESI-MS (MeCN) *m/z* (calculated, found):$[L+ H^+]$(483.36, 483.36).

diethyl (4-(icosyloxy)phenyl)phosphonate - $C_{30}H_{55}O_4P$ **(2F)**

Off-white waxy solid
Yield = 1.2g (67%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.69 (m, 2H, C**H**), 7.00 – 6.92 (m, 2H, C**H**), 4.19 – 3.97 (m, 6H, C$\mathbf{H_2}$), 1.95 – 1.74 (m, 4H, C$\mathbf{H_2}$), 1.55 – 1.19 (m, 39H, C$\mathbf{H_2}$/C$\mathbf{H_3}$), 0.90 (t, *J* = 6.9 Hz, 3H, C$\mathbf{H_3}$). ^{31}P NMR (202 MHz, $CDCl_3$) δ 19.90.
ESI-MS (MeCN) *m/z* (calculated, found):$[L+H^+]$(511.39, 511.38).

Step 3 – Phosphonate hydrolysis



Dried **2A-F** (quantity given below) was added to a 100ml Schlenk flask. The vessel was evacuated and filled with argon. To the vessel, dry dichloromethane (6 mL) was added followed by bromotrimethylsilane (TMSBr) (quantity given below) to form a yellow/green solution. The solution was then stirred for 20 h at 30°C. Upon completion, the vessel was cooled to room temperature and the solvent and excess TMSBr was removed *in vacuo* to yield a yellow oil. To the flask, 30 mL of methanol:water (80:20) was then added and stirred for 2 hours to form a white suspension. The mixture was then centrifuged (5 mins, 7000rpm) and the solvent was decanted off. The resulting solid was dried under vacuum to yield a crude off-white solid.

For compound **3A,** the crude product was then recrystallized from minimal amount of hot acetonitrile (30 mL) and filtered.

For compounds **3B-F** the crude product was then washed with diethyl ether (2 x 25 mL). The solid was then stirred in hot acetonitrile (50 mL) and filtered.

(4-(decyloxy)phenyl)phosphonic acid - $C_{16}H_{27}O_4P$ **(3A)**

2A: 1g, 2.7mmol
TMSBr: 1.95 ml, 14.78 mmol
White powder
Yield: 0.82 g, 96%
^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.81 – 7.62 (m, 2H, C**H**), 7.01 (dd, *J* = 8.7, 3.1 Hz, 2H, C**H**), 4.07 (t, *J* = 6.5 Hz, 2H, C$\mathbf{H_2}$), 1.81 (dq, *J* = 8.2, 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.54 – 1.42 (m, 2H, C$\mathbf{H_2}$), 1.39 – 1.24 (m, 14H, C$\mathbf{H_2}$), 0.97 – 0.76 (m, 3H, C$\mathbf{H_3}$); ^{31}P NMR (162 MHz, DMSO-d_6) δ 13.43.
IR(ATR) cm^{-1} = 447, 542, 686, 826, 942, 1012, 1140, 1255, 1294, 1474, 1504, 1599, 2852, 2918
Elemental Analysis: (Calculated, found) [(C, 61.13; H, 8.66; N, 0 %), (C, 59.61; H, 8.79; N, 0.05 %)];
ESI-MS (MeCN) *m/z* (calculated, found): $[L - H]^-$ (313.16, 313.16).

(4-(dodecyloxy)phenyl)phosphonic acid - $C_{18}H_{31}O_4$ **(3B)**

2B: 0.95g, 2.33 mmol
TMSBr: 1.84ml, 13.98
White powder
Yield: 0.72g, 90%
^{1}H NMR (400 MHz, Methanol-d_4) δ 7.83 – 7.65 (m, 2H, C**H**), 7.01 (dd, *J* = 8.7, 3.0 Hz, 2H, C**H**), 4.04 (t, *J* = 6.4 Hz, 2H, C$\mathbf{H_2}$), 1.85 – 1.74 (m, 2H, C$\mathbf{H_2}$), 1.32 (s, 18H, C$\mathbf{H_2}$), 0.97 – 0.87 (m, 3H, C$\mathbf{H_3}$); ^{31}P NMR (162 MHz, Methanol-d_4) δ 17.14.
IR(ATR) cm^{-1} = 451, 540, 686, 826, 943. 1014, 1142, 1250, 1474, 1504, 1599, 2850, 2918
Elemental Analysis: (Calculated, found) [(C, 63.14; H, 9.13; N, 0 %), (C, 62.76; H, 9.39; N, 0.07 %)]
ESI-MS (MeCN) *m/z* (calculated, found): $[L-H]^-$ (341.17,341.18).

(4-(tetradecyloxy)phenyl)phosphonic acid - $C_{20}H_{35}O_4P$ **(3C)**

2C: 0.92g, 2.16 mmol
TMSBr: 1.7ml, 12.96
White powder
Yield = 0.74g, 92%
^{1}H NMR (400 MHz, Methanol-d_4) δ 7.80 – 7.65 (m, 2H, C**H**), 7.08 – 6.94 (m, 2H, C**H**), 4.04 (t, *J* = 6.4 Hz, 2H, C$\mathbf{H_2}$), 1.88 – 1.75 (m, 2H, C$\mathbf{H_2}$), 1.31 (d, *J* = 2.2 Hz, 22H, C$\mathbf{H_2}$), 1.00 – 0.81 (m, 3H, C$\mathbf{H_3}$); ^{31}P NMR (162 MHz, Methanol-d_4) δ 17.18.
IR(ATR) cm^{-1} = 451, 542, 686, 826, 946, 1022, 1144, 1253, 1292, 1476, 1504, 1599, 2850, 2916
Elemental Analysis: (Calculated, found) [(C, 64.84; H, 9.52; N, 0 %), (C,64.91; H,9.81; N,0.06 %)]
ESI-MS (MeCN) *m/z* (calculated, found): [L-H]$^-$ (369.22,369.22)

(4-(hexadecyloxy)phenyl)phosphonic acid - $C_{22}H_{39}O_4P$ **(3D)**

2D: 1.66 g, 3.49 mmol
TMSBr: 3 ml, 22.59 mmol
White powder
Yield = 1.17 g, 84%
^{1}H NMR (400 MHz, Methanol-d_4) δ 7.81 – 7.65 (m, 2H, C**H**), 7.01 (dd, *J* = 8.7, 3.1 Hz, 2H, C**H**), 4.04 (t, *J* = 6.5 Hz, 2H, C$\mathbf{H_2}$), 1.81 (p, *J* = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.31 (d, *J* = 2.6 Hz, 26H, C$\mathbf{H_2}$), 0.96 – 0.88 (m, 3H, C$\mathbf{H_3}$);^{31}P NMR (162 MHz, Methanol-d_4) δ 17.23.
IR(ATR) cm^{-1} = 455, 544, 688, 826, 944, 1020, 1144, 1253, 1474, 1253, 1506, 1599, 2850, 2916
Elemental Analysis: [(C, 66.31; H, 9.86; N, 0 %), (C,66.37; H,10.12; N,0.08 %)]
ESI-MS (MeCN) *m/z* (calculated, found): [L-H]$^-$ (397.25, 397.25).

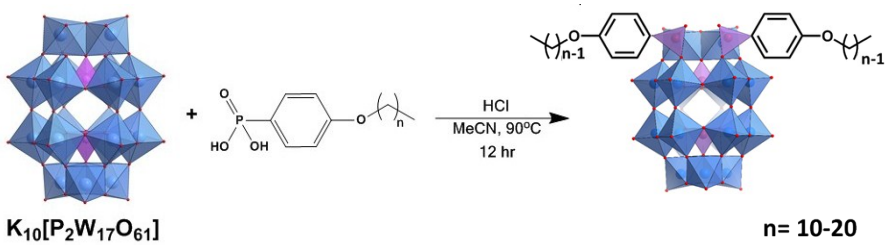
(4-(octadecyloxy)phenyl)phosphonic acid - $C_{24}H_{43}O_4P$ **(3E)**

2E: 1.04 g, 2.07 mmol
TMSBr: 1.95 ml, 14.78 mmol
White powder
Yield = 0.84 g, 96 %
^{1}H NMR (500 MHz, Methanol-d_4) δ 7.80 – 7.68 (m, 2H, C**H**), 7.01 (dq, *J* = 9.3, 2.7 Hz, 2H, C**H**), 4.04 (t, *J* = 6.5 Hz, 2H, C$\mathbf{H_2}$), 1.89 – 1.74 (m, 2H, C$\mathbf{H_2}$), 1.31 (d, *J* = 4.8 Hz, 30H, C$\mathbf{H_2}$), 0.92 (t, *J* = 6.9 Hz, 3H, C$\mathbf{H_3}$);^{31}P NMR (202 MHz, Methanol-d_4) δ 17.27.
IR(ATR) cm^{-1} = 449, 542, 686, 826, 946, 1020, 1142, 1255, 1463, 1506, 1599, 2850, 2918
Elemental Analysis: [(C, 67.58; H, 10.16; N, 0 %), (C,67.51; H,10.49; N,0.08 %)]
ESI-MS (MeCN) *m/z* (calculated, found): [L-H]$^-$ (425.29,425.29).

(4-(icosyloxy)phenyl)phosphonic acid - $C_{26}H_{47}O_4P$ **(3F)**

2F: 0.99 g, 1.95 mmol
TMSBr: 1 ml, 7.35 mmol
White powder
Yield = 0.85 g, 96 %
^{1}H NMR (400 MHz, Methanol-d_4) δ 7.78 – 7.66 (m, 2H, C**H**), 7.01 (dd, *J* = 8.7, 3.1 Hz, 2H, C**H**), 4.04 (t, *J* = 6.4 Hz, 2H, C$\mathbf{H_2}$), 1.81 (p, *J* = 6.6 Hz, 2H, C$\mathbf{H_2}$), 1.31 (d, *J* = 3.7 Hz, 34H, C$\mathbf{H_2}$), 0.96 – 0.86 (m, 3H, C$\mathbf{H_3}$);^{31}P NMR (162 MHz, Methanol-d_4) δ 17.27.
IR(ATR) cm^{-1} = 457, 544, 684, 719, 828, 946, 1020, 1146, 1252, 1294, 1463, 1506, 1601, 2848, 2916
Elemental Analysis: [(C, 68.69; H, 10.42; N, 0 %), (C,68.74; H,10.81; N,0.09 %)];
ESI-MS (MeCN) *m/z* (calculated, found): [L-H]$^-$(453.63, 453.34).

Step 4 – Hybridisation



$K_{10}[P_2W_{17}O_{61}]$ n= 10-20

3A-F (0.33 mmol) and $K_{10}[P_2W_{17}O_{61}]$ (0.5g, 0.11 mmol) were suspended in acetonitrile (50 ml) and 12 M HCl (37 wt. %, 0.14 mL). The reaction mixture was stirred at 90°C for 24 h to form a yellow solution. Upon completion, the reaction was cooled to room temperature and filtered. The solvent was then evaporated *in vacuo,* resulting in an orange solid. The solid was then re-dissolved in cold acetone and left overnight in the fridge. The cold solution was then centrifuged at 8000 rpm for 15 mins. The yellow solution was then filtered, and the solvent removed *in vacuo* to form a dark red powder. The solid was then sonicated in diethyl ether (2 x 100 mL) and decanted. The remaining solvent was removed *in vacuo*.

$K_6[P_2W_{17}O_{61}(PO_2C_6H_4(C_{10}H_{21})_2]$ **({$W_{17}C_{10}$})**
Red powder
Yield = 0.4g (74%)
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 – 7.85 (m, 4H, C**H**), 6.98 (td, *J* = 8.8, 3.1 Hz, 4H, C**H**), 4.03 (t, *J* = 6.4 Hz, 4H, C$\mathbf{H_2}$), 1.74 (t, *J* = 7.3 Hz, 4H, C$\mathbf{H_2}$), 1.43 – 1.20 (m, 28H, C$\mathbf{H_2}$), 0.87 (t, *J* = 6.7 Hz, 6H, C$\mathbf{H_3}$).^{31}P NMR (202 MHz, DMSO-d_6) δ 15.94, -11.37, -13.00.
IR(ATR) cm^{-1} = 525, 719, 803, 903, 954, 1084, 1136, 1251, 1504, 1597, 2850, 2920.
Elemental analysis for **{$W_{17}C_{10}$}** in wt. %(calculated): C 8.07(7.75), H 1.24 (1.02).

$K_6[P_2W_{17}O_{61}(PO_2C_6H_4(C_{12}H_{25})_2]$ **({$W_{17}C_{12}$})**
Red powder
Yield = 0.38g (70%)
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.00 – 7.83 (m, 4H, **CH**), 6.98 (td, *J* = 8.9, 4.5 Hz, 4H, **CH**), 4.02 (dt, *J* = 16.8, 6.5 Hz, 4H, $\mathbf{CH_2}$), 1.78 – 1.71 (m, 4H, $\mathbf{CH_2}$), 1.47 – 1.20 (m, 36H, $\mathbf{CH_2}$), 0.90 – 0.83 (m, 6H, $\mathbf{CH_3}$).^{31}P NMR (202 MHz, DMSO-d_6) δ 15.93 (t, *J* = 13.4 Hz), -11.37, -13.00.
IR(ATR) cm^{-1} = 525, 570, 717, 799, 905, 954, 1086, 1138, 1261, 1504, 1597, 1696, 2848, 2922.
Elemental analysis for **{$W_{17}C_{12}$}** in wt. % (calculated): C 8.91(8.62), H 1.24 (1.17).

$K_6[P_2W_{17}O_{61}(PO_2C_6H_4(C_{14}H_{29})_2]$ **({$W_{17}C_{14}$})**
Red powder
Yield = 0.39g (71%)
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 – 7.84 (m, 4H, C**H**), 6.98 (dt, *J* = 10.0, 5.0 Hz, 4H, C**H**), 4.05 – 4.01 (m, 4H, C$\mathbf{H_2}$), 1.73 (d, *J* = 7.5 Hz, 4H, C$\mathbf{H_2}$), 1.47 – 1.22 (m, 44H, C$\mathbf{H_2}$), 0.86 (t, *J* = 6.7 Hz, 6H, C$\mathbf{H_3}$).^{31}P NMR (162 MHz, DMSO-d_6) δ 15.94, -11.37, -13.00.
IR(ATR) cm^{-1} = 530, 570, 719, 793, 901, 955, 1086, 1136, 1261, 1506, 1599, 2854, 2916.
Elemental analysis for **{$W_{17}C_{14}$}** in wt. % (calculated): C 10.13 (9.47), H 1.44 (1.31).

$K_6[P_2W_{17}O_{61}(PO_2C_6H_4(C_{16}H_{33})_2]$ (**{$W_{17}C_{16}$}**)
Red powder
Yield = 0.43g (77%)
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (dd, *J* = 13.5, 8.5 Hz, 4H, C**H**), 6.99 (dd, *J* = 9.1, 3.1 Hz, 4H, C**H**), 4.03 (t, *J* = 6.5 Hz, 4H, C**H$_2$**), 1.73 (d, *J* = 7.4 Hz, 4H, C**H$_2$**), 1.26 (d, *J* = 6.4 Hz, 52H C**H$_2$**), 0.89 – 0.84 (m, 6H, C**H$_3$**).^{31}P NMR (162 MHz, DMSO-d_6) δ 15.93, -11.37, -13.00.
IR(ATR) cm^{-1} = 528, 567, 731, 905, 954, 1086, 1138, 1255, 1597, 2852, 2918.
Elemental analysis for **{$W_{17}C_{16}$}** in wt. % (calculated): C 11.35 (10.30), H 1.63 (1.45).

$K_6[P_2W_{17}O_{61}(PO_2C_6H_4(C_{18}H_{37})_2]$ (**{$W_{17}C_{18}$}**)
Red powder
Yield = 0.43g (76%)
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (ddd, *J* = 33.5, 13.5, 8.4 Hz, 4H, C**H**), 6.98 (dt, *J* = 10.2, 5.1 Hz, 4H, C**H**), 4.01 (dt, *J* = 13.2, 6.5 Hz, 4H, C**H$_2$**), 1.76 – 1.64 (m, 4H C**H$_2$**), 1.25 (s, 60H, C**H$_2$**), 0.90 – 0.82 (m, 6H, C**H$_3$**). ^{31}P NMR (162 MHz, DMSO-d_6) δ 15.93, -11.37, -13.00.
IR(ATR) cm^{-1} = 528, 567, 721, 798, 909, 956, 1088, 1138, 1260, 1595, 2852, 2922.
Elemental analysis for **{$W_{17}C_{18}$}** in wt. % (calculated): C 11.22 (11.11), H 1.61 (1.59).

$K_6[P_2W_{17}O_{61}(PO_2C_6H_4(C_{20}H_{41})_2]$ (**{$W_{17}C_{20}$}**)
Red powder
Yield = 0.42g (73%)
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 – 7.84 (m, 4H, C**H**), 6.98 (td, *J* = 9.2, 3.2 Hz, 4H, C**H**), 4.01 (dt, *J* = 13.4, 6.4 Hz, 4H, C**H$_2$**), 1.78 – 1.68 (m, 4H, C**H$_2$**), 1.24 (s, 68H, C**H$_2$**), 0.90 – 0.82 (m, 6H, C**H$_3$**).^{31}P NMR (162 MHz, DMSO-d_6) δ 15.95 (d, *J* = 3.5 Hz), -11.36, -12.99.
IR(ATR) cm^{-1} = 525, 562, 708, 795, 907, 956, 1088, 1136, 1255, 1597, 2852, 2920.
Elemental analysis for **{$W_{17}C_{20}$}** in wt. % (calculated): C 11.97 (11.91), H 1.75 (1.73).

Mass-spectrometry

{$W_{17}C_{10}$}

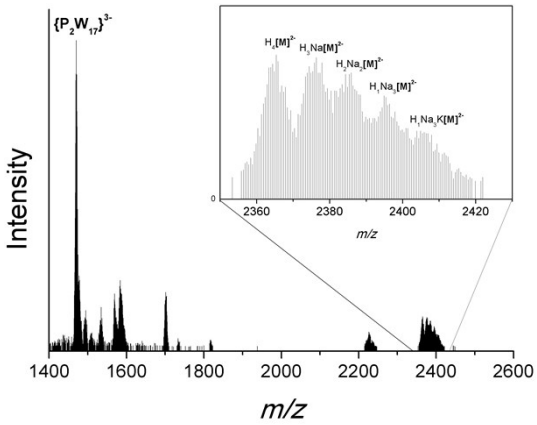


Figure S1 – High resolution ESI mass spectrum of ***{$W_{17}C_{10}$}***

Assignment	z	*m/z (calc.)*	*m/z (obs.)*
$P_2W_{17}O_{61}$ $(PO_2C_{16}H_{25})_2H_4$	2-	2364.1	2364.3
$P_2W_{17}O_{61}$ $(PO_2C_{16}H_{25})_2$ NaH_3	2-	2375.1	2375.3
$P_2W_{17}O_{61}$ $(PO_2C_{16}H_{25})_2Na_2H_2$	2-	2386.1	2386.4
$P_2W_{17}O_{61}$ $(PO_2C_{16}H_{25})_2Na_3H$	2-	2397.1	2397.4
$P_2W_{17}O_{61}$ $(PO_2C_{16}H_{25})_2KNa_2H$	2-	2405.0	2405.4
$P_2W_{17}O_{61}$ $(PO_2C_{16}H_{25})_0K_4H_3(H_2O)_5$	3-	1407.9	1407.6

{$W_{17}C_{12}$}

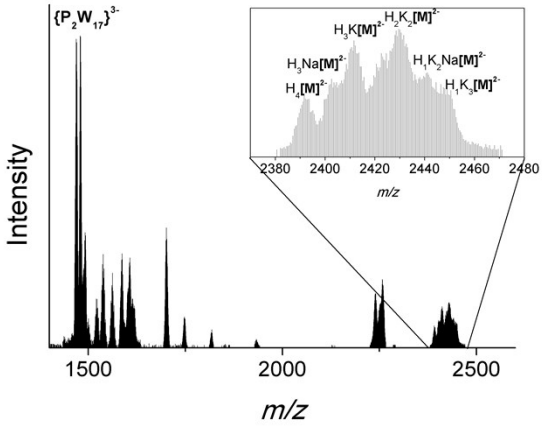


Figure S2 - High resolution ESI mass spectrum of ***{$W_{17}C_{12}$}***

Assignment	z	*m/z (calc.)*	*m/z (obs.)*
$P_2W_{17}O_{61}$ $(PO_2C_{18}H_{29})_2H_4$	2-	2392.1	2392.1
$P_2W_{17}O_{61}$ $(PO_2C_{18}H_{29})_2NaH_3$	2-	2403.1	2403.1
$P_2W_{17}O_{61}$ $(PO_2C_{18}H_{29})_2KNaH_3$	2-	2411.1	2411.1
$P_2W_{17}O_{61}$ $(PO_2C_{18}H_{29})_2$ K_2H_2	2-	2430.1	2430.1
$P_2W_{17}O_{61}$ $(PO_2C_{18}H_{29})_2$ K_3H	2-	2449.0	2449.1
$P_2W_{17}O_{61}$ $(PO_2C_{18}H_{29})_2$ K_2NaH	2-	2441.1	2441.1
$P_2W_{17}O_{61}$ $(PO_2C_{18}H_{29})_0K_6Na(H_2O)$	3-	1479.5	1479.7

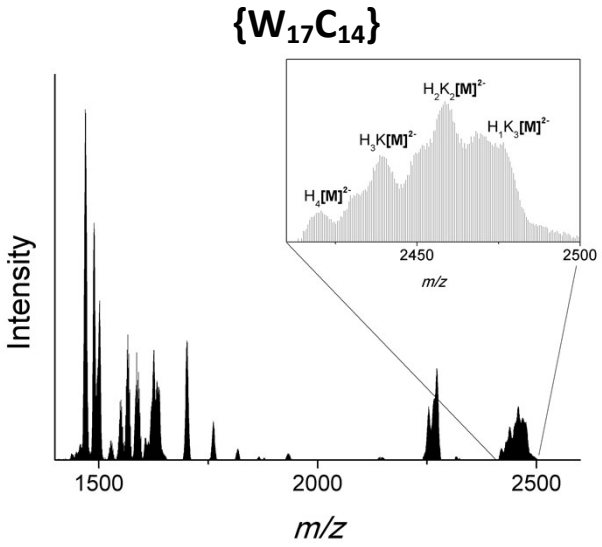


Figure S3 - High resolution ESI mass spectrum of ***{$W_{17}C_{14}$}***

Assignment	z	*m/z (calc.)*	*m/z (obs.)*
$P_2W_{17}O_{61}(PO_2C_{26}H_{45})_2H_4$	2-	2420.1	2420.1
$P_2W_{17}O_{61}(PO_2C_{26}H_{45})_2K_1H_3$	2-	2439.1	2439.1
$P_2W_{17}O_{61}(PO_2C_{26}H_{45})_2K_2H_2$	2-	2458.1	2458.1
$P_2W_{17}O_{61}(PO_2C_{26}H_{45})_2K_3H$	2-	2477.1	2477.1

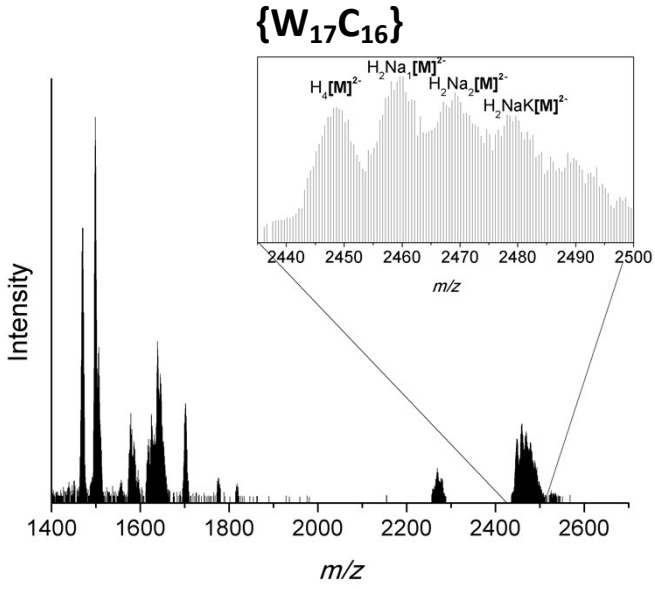


Figure S4 - High resolution ESI mass spectrum of ***{$W_{17}C_{16}$}***

Assignment	z	*m/z (calc.)*	*m/z (obs.)*
$P_2W_{17}O_{61}(PO_2C_{22}H_{37})_0\ K_4\ Na_3(H_2O)_6$	3-	1498.9	1499.0
$P_2W_{17}O_{61}(PO_2C_{22}H_{37})_2H_4$	2-	2248.2	2248.2
$P_2W_{17}O_{61}(PO_2C_{22}H_{37})_2NaH_3$	2-	2459.2	2459.2
$P_2W_{17}O_{61}(PO_2C_{22}H_{37})_2\ KH_3$	2-	2467.1	2467.2
$P_2W_{17}O_{61}(PO_2C_{22}H_{37})_2Na_2H_2$	2-	2470.2	2470.1
$P_2W_{17}O_{61}(PO_2C_{22}H_{37})_2KNaH_2$	2-	2478.1	2478.1

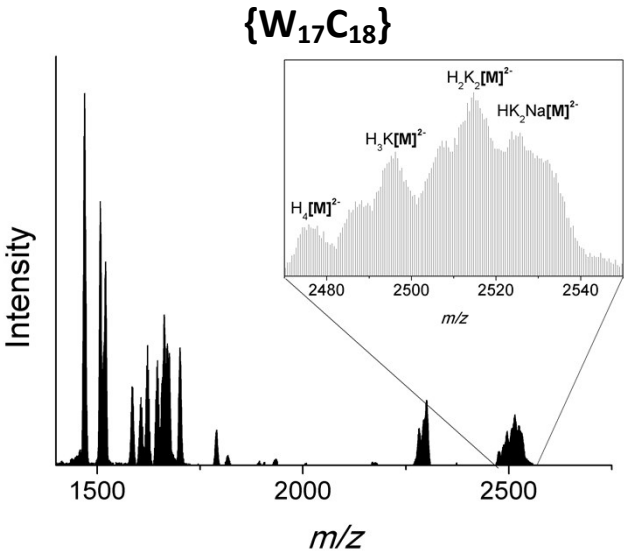


Figure S5 - High resolution ESI mass spectrum of ***{$W_{17}C_{18}$}***

Assignment	z	*m/z (calc.)*	*m/z (obs.)*
$P_2W_{17}O_{61}(P_1O_2C_{24}H_{41})_2H_4$	2-	2476.2	2476.3
$P_2W_{17}O_{61}(P_1O_2C_{24}H_{41})_2K_1H_3$	2-	2495.2	2495.2
$P_2W_{17}O_{61}(P_1O_2C_{24}H_{41})_2K_2H_2$	2-	2514.2	2514.2
$P_2W_{17}O_{61}(P_1O_2C_{24}H_{41})_2K_2Na_1H_1$	2-	2525.2	2525.2
$P_2W_{17}O_{61}(P_1O_2C_{24}H_{41})_2K_3H_1$	2-	2533.1	2533.2

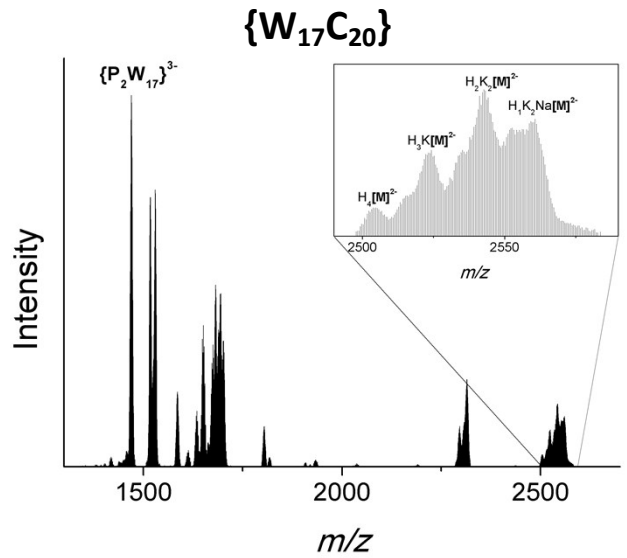


Figure S6 - High resolution ESI mass spectrum of ***{$W_{17}C_{20}$}***

Assignment	z	*m/z (calc.)*	*m/z (obs.)*
$P_2W_{17}O_{61}$ $(PO_2C_{26}H_{45})_2H_4$	2-	2504.2	2504.3
$P_2W_{17}O_{61}$ $(PO_2C_{26}H_{45})_2NaH_3$	2-	2515.2	2515.3
$P_2W_{17}O_{61}$ $(PO_2C_{26}H_{45})_2KH_3$	2-	2523.2	2523.3
$P_2W_{17}O_{61}$ $(PO_2C_{26}H_{45})_2KNaH_2$	2-	2534.2	2534.2
$P_2W_{17}O_{61}$ $(PO_2C_{26}H_{45})_2K_2H_2$	2-	2542.2	2542.2
$P_2W_{17}O_{61}$ $(PO_2C_{26}H_{45})_2K_2NaH$	2-	2553.2	2553.2

NMR characterisation

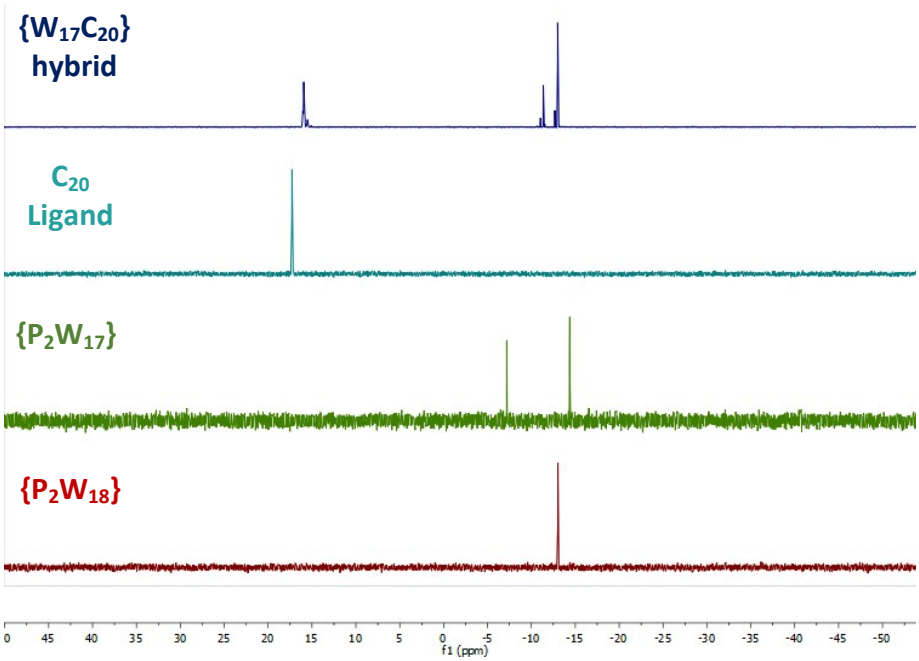


*Figure S7 – ^{31}P NMR spectra of **{$W_{17}C_{20}$}** in d_6-DMSO, the organophosphonate C_{20} ligand **(3F)** in d_6-DMSO, the parent lacunary POM cluster $K_{10}[P_2W_{17}O_{61}]$ (**{P_2W_{17}}**) and the parent Wells-Dawson POM cluster $K_6[P_2W_{18}O_{62}]$ (**{P_2W_{18}}**).*

FT-IR analysis

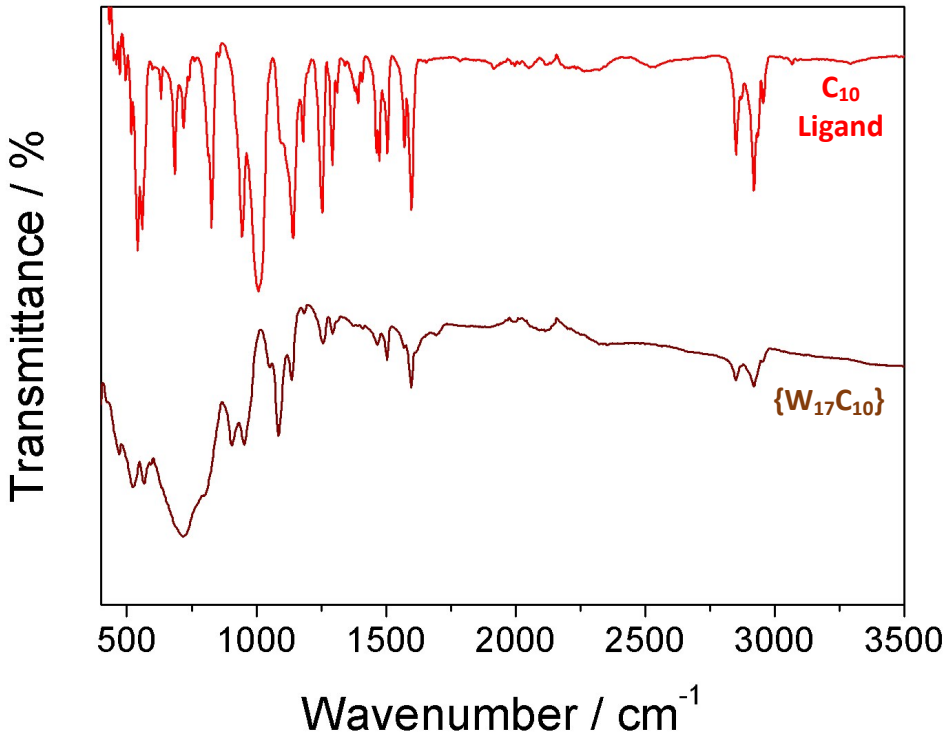


*Figure S8 – An IR spectrum comparing the C_{10} phosphonic acid ligand (red) to the hybrid **{$W_{17}C_{10}$}** molecule (brown). Signals for both compounds are representative of the compound series as a whole (full assignments given in the experimental section above).*

Absorption spectroscopy (UV-Vis)

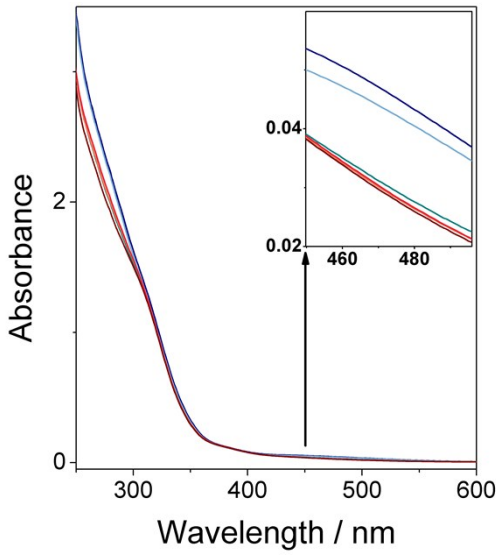


Figure S9 - UV-VIS spectra of ***{W$_{17}$C$_{10-20}$}*** *in H_2O (50 µM).*

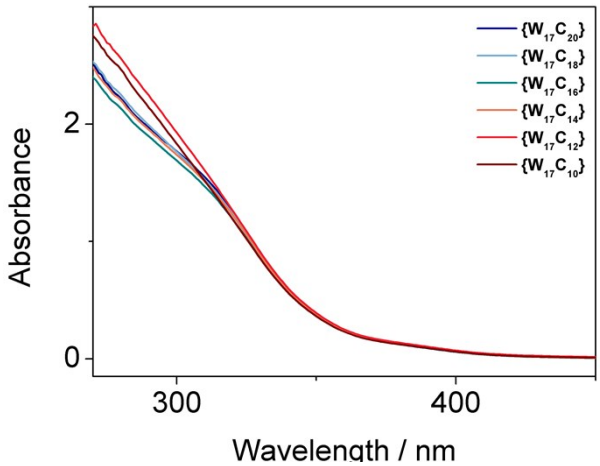


Figure S10 – UV-VIS spectra of ***{W$_{17}$C$_{10-20}$}*** *in DMF (50 µM).*

Electrochemistry and DLS

Cyclic voltammetry (CV) experiments under non-aqueous conditions were performed using a CHI instruments potentiostat using a standard three-electrode arrangement: working electrode: glassy carbon, d= 3mm; reference electrode: Ag wire, and; counter electrode: Pt wire. All potentials are quoted versus ferrocene, which was used as an internal standard. TBA.PF_6 (0.1M) was used as the supporting electrolyte and dry *N,N'*-dimethylformamide (DMF) was used as the solvent. All solutions were purged with argon for 10 mins prior to measurement and kept under a positive pressure of Ar for the duration of the experiment. All measurements were performed at a scan rate of 100 mV s^{-1}.

CV experiments conducted under aqueous conditions (including those where DMF was subsequently added) were performed using a CHI potentiostat with a three-electrode setup: working electrode: glassy carbon, d= 3mm; reference electrode: Ag/AgCl, and; counter electrode: Pt wire. All potentials are quoted relative to Ag/AgCl. Dilute (0.1M) H_2SO_4 was used as the supporting electrolyte. All solutions were purged with argon for 10 mins and kept under a positive pressure of Argon for the duration of the experiment. All measurements were performed at a scan rate of 100 mV s^{-1}.

Dynamic light scattering (DLS) studies of the unadulterated electrochemical solutions were performed using a Malvern Zetasizer Nano ZS.

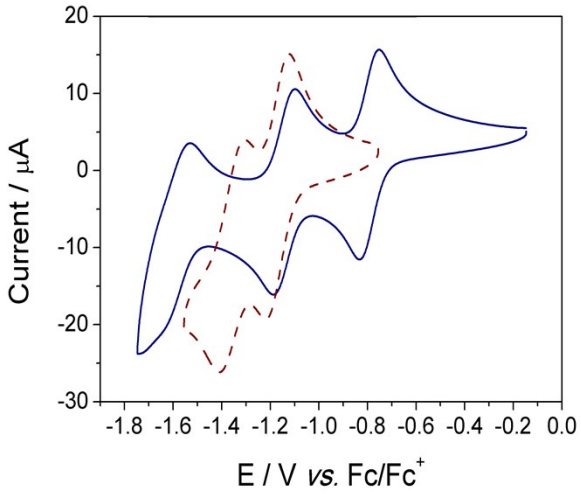


Figure S11 - A cyclic voltamagram of ***{P_2W_{18}}*** *(red) and* ***{$W_{17}C_{20}$}*** *(navy blue) (1.4 mM) in DMF with 0.1M TBA.PF_6 as the supporting electrolyte.*

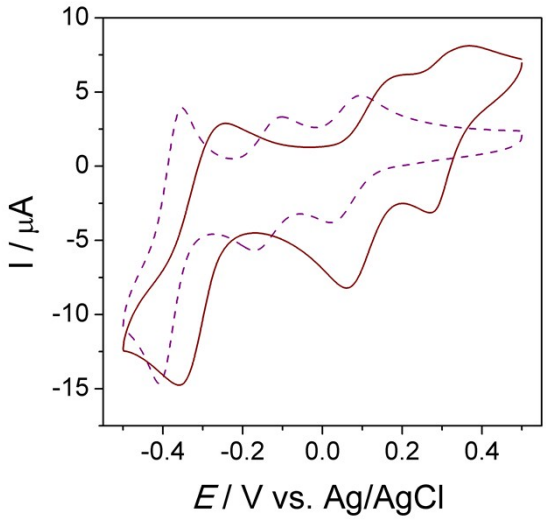


Figure S12 - Cyclic voltammogram of ***{$W_{17}C_{10}$}*** *in aqueous conditions (i.e. in the micellar form; maroon line), and upon addition of DMF (i.e. in the molecular form, purple dashed line) vs. Ag/AgCl.*

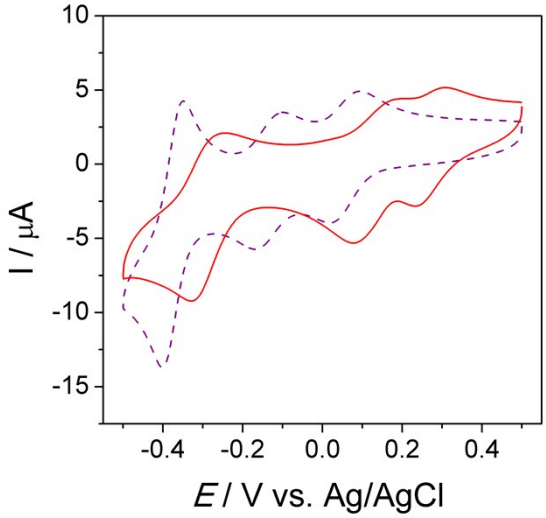


Figure S13 - Cyclic voltammogram of ***{$W_{17}C_{12}$}*** *in aqueous conditions (i.e. in the micellar form; red line), and upon addition of DMF (i.e. in the molecular form, purple dashed line) vs. Ag/AgCl.*

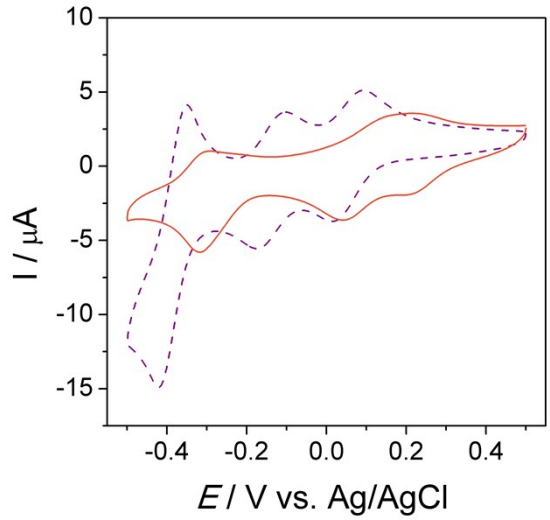


Figure S14 - Cyclic voltammogram of ***{W$_{17}$C$_{14}$}*** *in aqueous conditions (i.e. in the micellar form; orange line), and upon addition of DMF (i.e. in the molecular form, purple dashed line) vs. Ag/AgCl.*

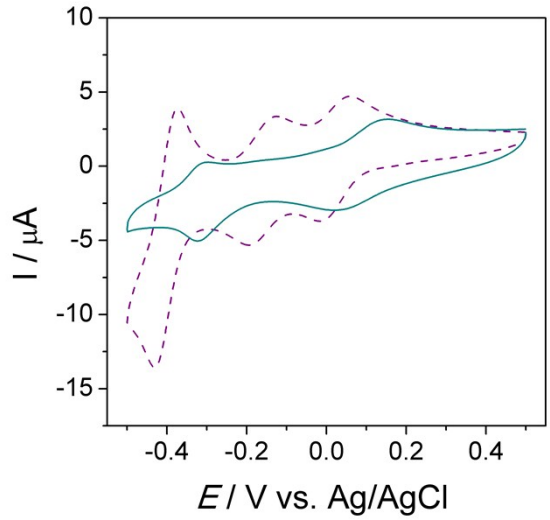


Figure S15 - Cyclic voltammogram of ***{W$_{17}$C$_{16}$}*** *in aqueous conditions (i.e. in the micellar form; teal line), and upon addition of DMF (i.e. in the molecular form, purple dashed line) vs. Ag/AgCl.*

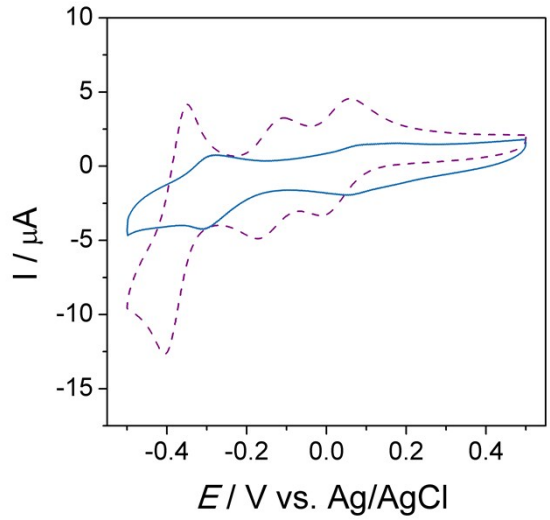


Figure S16 - Cyclic voltammogram of ***{$W_{17}C_{18}$}*** *in aqueous conditions (i.e. in the micellar form; blue line), and upon addition of DMF (i.e. in the molecular form, purple dashed line) vs. Ag/AgCl.*

	$E_{1/2}$ / V vs. Ag/AgCl					
	0.1M H_2SO_4			0.1M H_2SO_4 + 2ml DMF		
	I/I*	**II/II***	**III**	**I**	**II**	**III**
{$W_{17}C_{10}$}	0.319	0.112	-0.301	0.057	-0.137	-0.382
{$W_{17}C_{12}$}	0.270	0.124	-0.294	0.056	-0.135	-0.376
{$W_{17}C_{14}$}	(-)†	0.129	-0.304	0.053	-0.139	-0.387
{$W_{17}C_{16}$}	0.0863	-0.311	-	0.021	-0.159	-0.402
{$W_{17}C_{18}$}	0.0697 (0.116)‡	-0.294	-	0.023	-0.141	-0.379
{$W_{17}C_{20}$}	0.0889 (0.157)§	-0.265	-	0.070	-0.0266	-0.353

† Note that an accurate $E_{1/2}$ value could not be assigned here due to the difficulty in assigning a (pseudo-)reversible wave owing to the coalescing of the oxidation waves into a single process.
‡ & **§** $E_{1/2}$ values corresponding to a pseudo-reversible process between the reduction and more positive oxidation waves.

Table S1 – Cyclic voltammetry $E_{1/2}$ values of micelles in 0.1M H_2SO_4 and micelles in 0.1M H_2SO_4 + DMF.

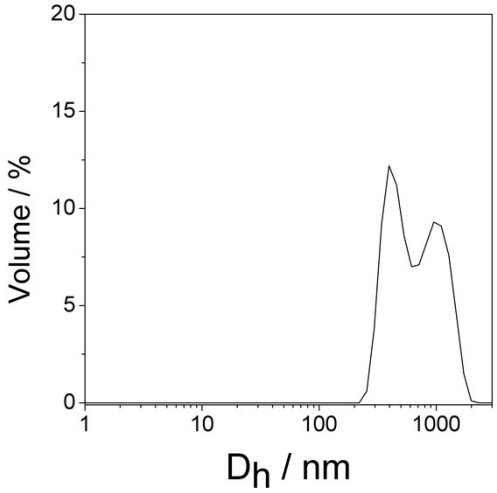


Figure S17 – DLS of ***{W$_{17}$C$_{20}$}*** *micelle solution (1.4mM) in 0.1M H_2SO_4 + 2ml DMF which displays no small micellar assemblies.*

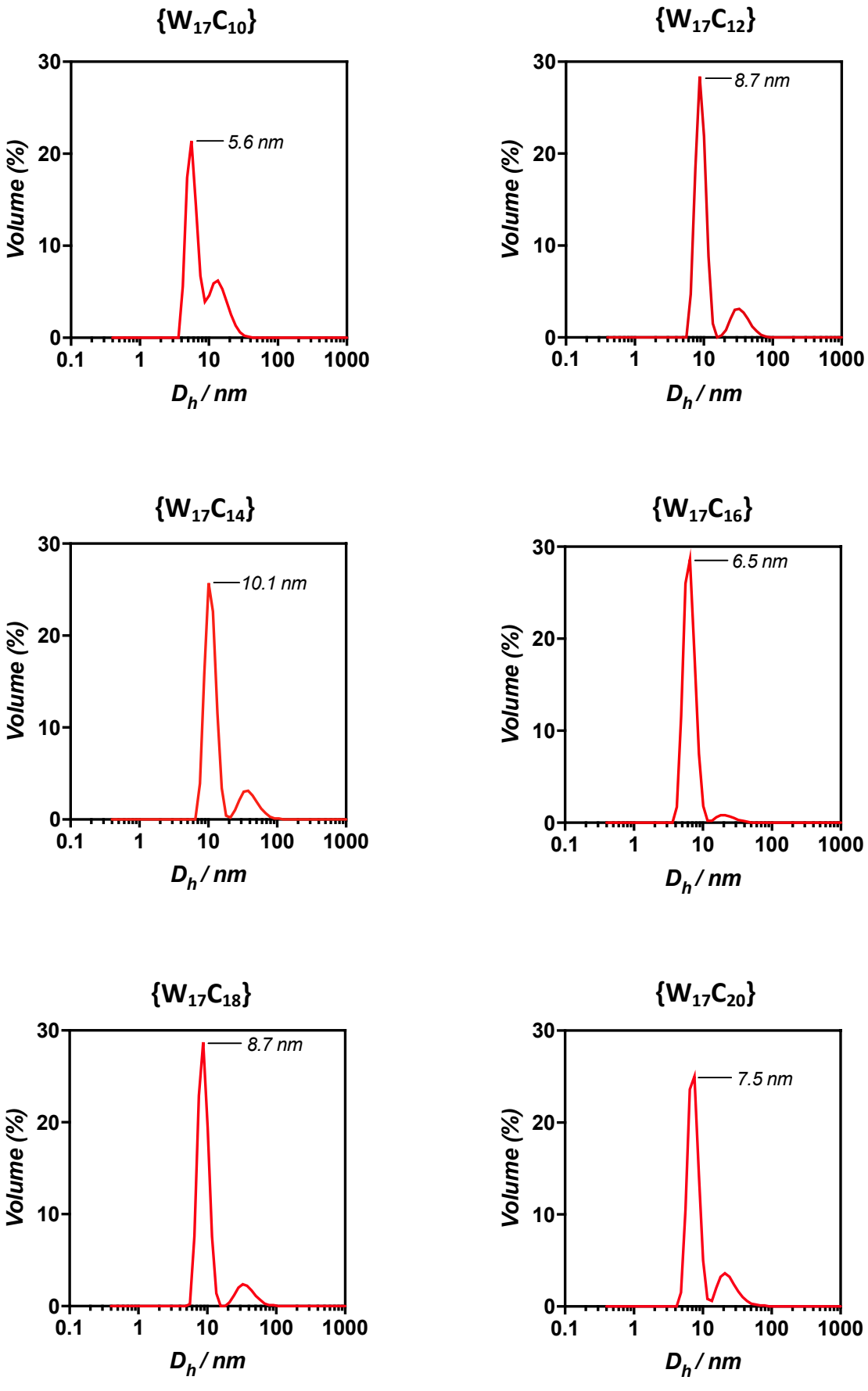


Figure S18 - Particle-size distribution analysis of ***{W17C10-20}*** *(1.4mM) in 0.1M H_2SO_4.*

Solvatochromism

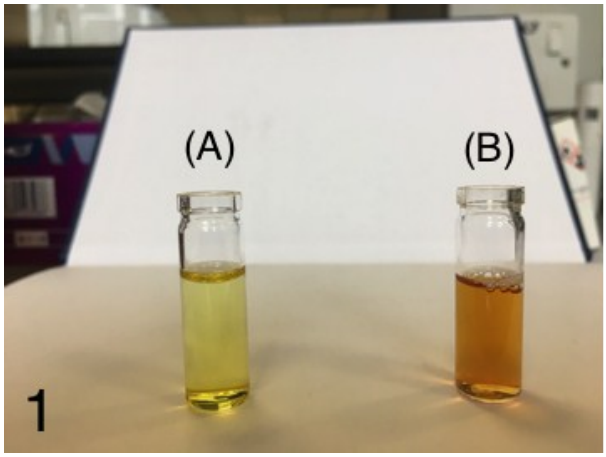


Figure S19 - Both vials contain ***{W$_{17}$C$_{10}$}*** *2mM in DMF (A) and H_2O (B).*

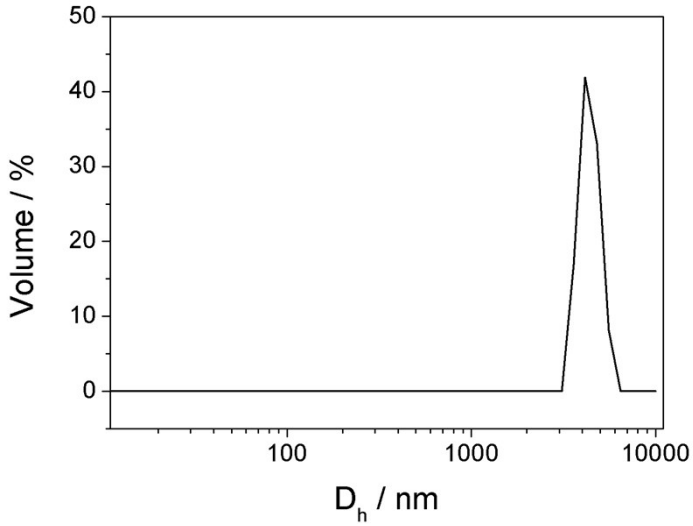


Figure S20 –DLS analysis of 1.4mM ***{W$_{17}$C$_{20}$}*** *in DMF which indicates no small nanoaggregates in solution. (Note that this behaviour is representative of all* ***{W$_{17}$C$_n$}*** *species dissolved in neat DMF.*

Critical Micelle Concentration (CMC)

The critical micelle concentration was analysed by measuring the size distribution of the surfactant water solutions at different concentrations. The approximate CMC was determined by observing a large jump from micellar sized assemblies to larger aggregates.

Compound	CMC (mol/dm^3)
{$W_{17}C_{10}$}	*n/a**
{$W_{17}C_{12}$}	1.4 x 10^{-3}
{$W_{17}C_{14}$}	1.2 x 10^{-3}
{$W_{17}C_{16}$}	1.0 x 10^{-3}
{$W_{17}C_{18}$}	7.5 x 10^{-4}
{$W_{17}C_{20}$}	7.5 x 10^{-4}

***{$W_{17}C_{10}$}** does not form stable micelles up to a concentration of 4.5 x 10^{-3} mol/dm^3, at which point it begins to precipitate from aqueous solution, forming a turbid suspension.

Thermogravimetric analysis (TGA)

Thermal gravimetric analysis of the C_{10}-POM surfactant is provided as a representative example of the thermal stability of all **{$W_{17}C_n$}** compounds. This is also in good agreement with the thermal properties of closely related hybrid polyoxometalate species reported elsewhere (see Kastner et al., *J. Mater. Chem. A*, 2017, **5**, 11577-11581).

{$W_{17}C_{10}$}

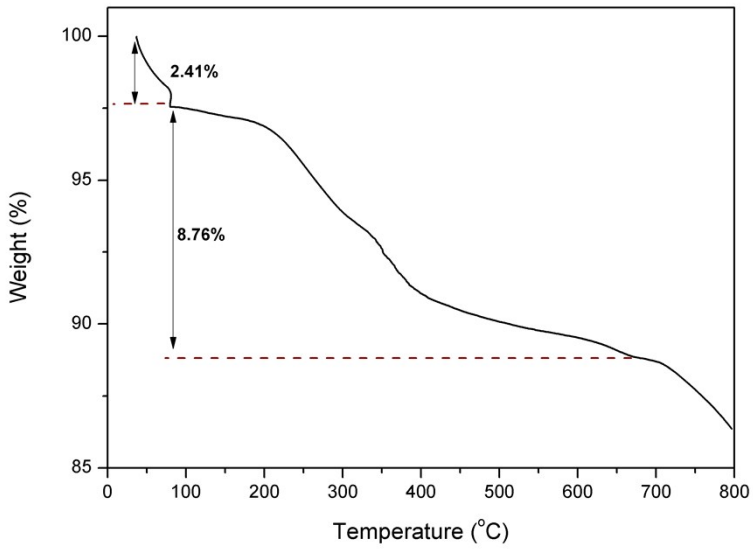


Figure S21 - TGA weight loss profile associated with {$W_{17}C_{10}$} shows an initial weight loss of 2.41% which is associated with the loss of 3 CH_3CN molecules and a second weight loss (T_o 240 °C) of 8.76 % (obs) associated with the loss of 2 two organic ligand moieties [-$C_{16}H_{25}O$] (calc. 9.41 %)

TEM analysis

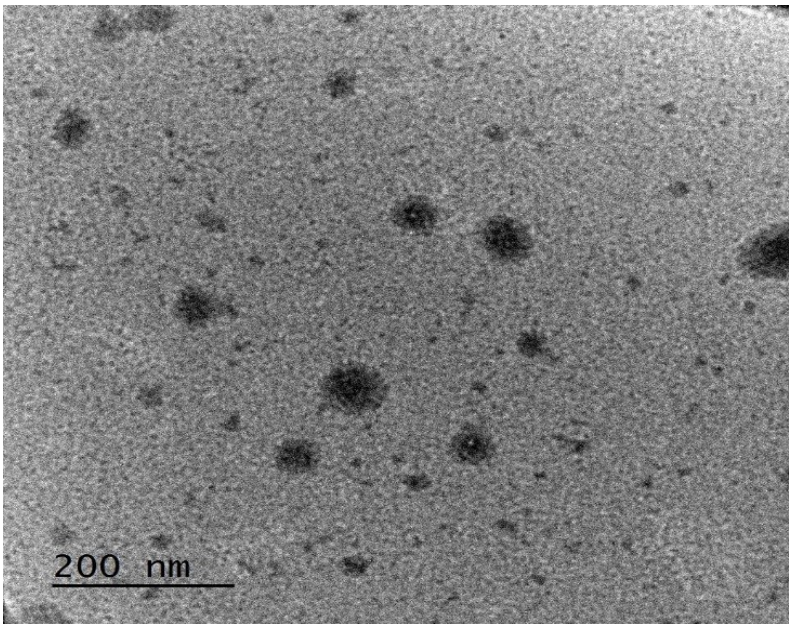


Figure S27 – TEM of ***{W$_{17}$C$_{10}$}*** *(1mM) in H_2O.*

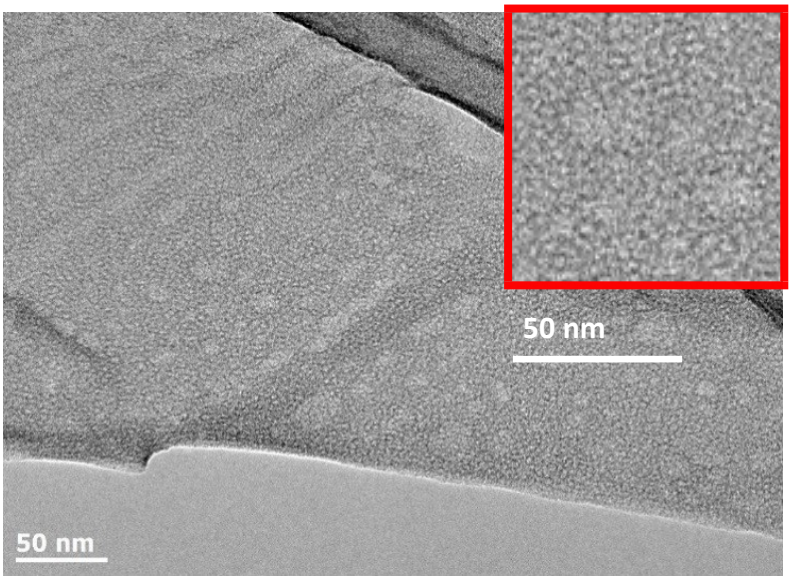


Figure S28 - TEM of ***{W$_{17}$C$_{12}$}*** *(1mM) in H_2O.*

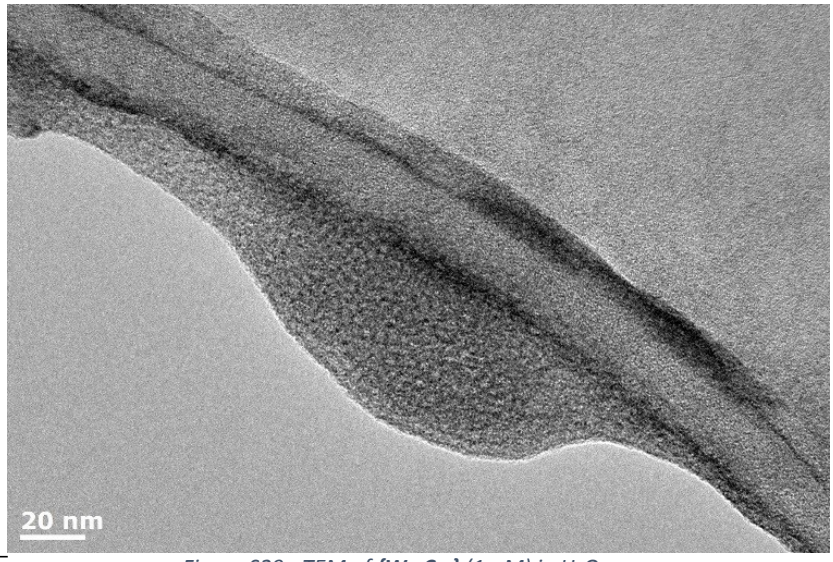


Figure S29 - TEM of ***{W$_{17}$C$_{14}$}*** *(1mM) in H$_2$O.*

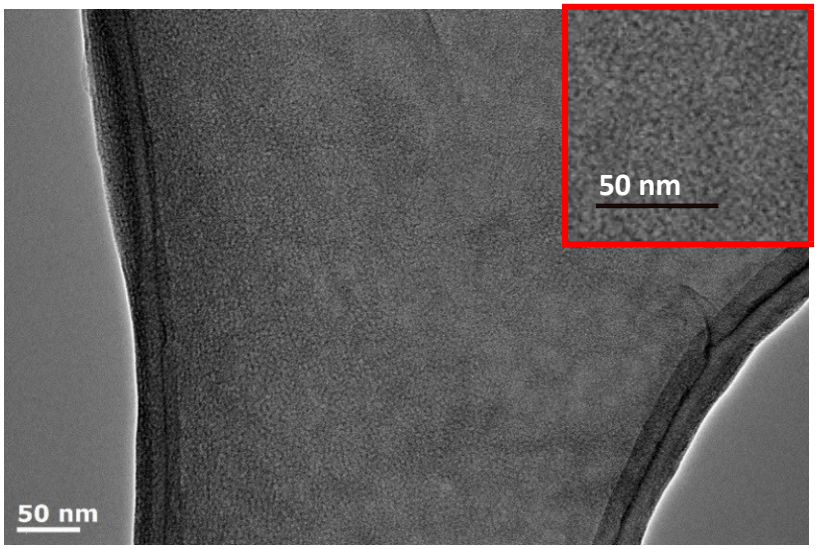


Figure S30 - TEM of ***{W$_{17}$C$_{16}$}*** *(1mM) in H$_2$O.*

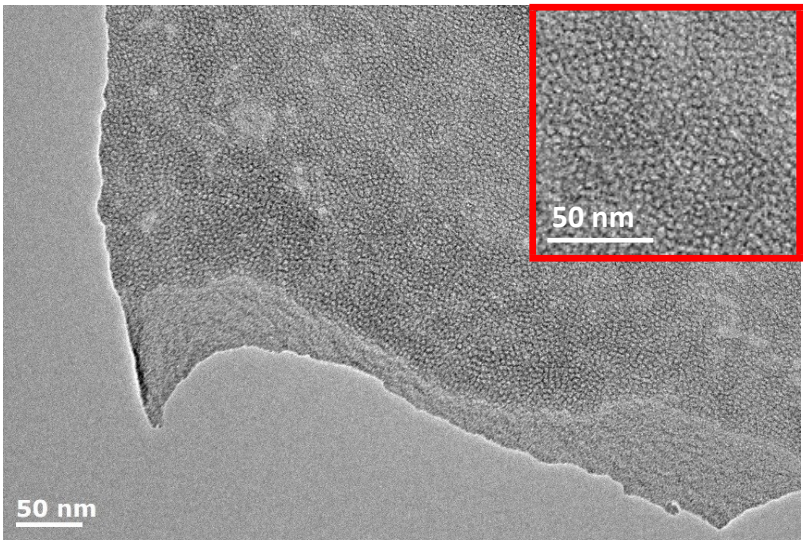


Figure S31 - TEM of ***{W$_{17}$C$_{20}$}*** *(1mM) in H$_2$O.*