Supporting Information

Redox-active Hierarchical Assemblies of Hybrid Polyoxometalate Nanostructures at Carbon Surfaces

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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 15 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.

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

SEM imaging - images were obtained using JEOL 7000F FEG SEM at an accelerating voltage of 15KV.

AFM - Tapping-mode AC-AFM images were taken using an Asylum Research Cypher-S instrument with NuNano Scout 70 probes. Those presented here consistent of topographical height channel responses, though phase and amplitude channel images were stored.

Ellipsometry was performed using an Acccurion ep4 imaging ellipsometer on an approx. 1cm square of glassy carbon that had been partially treated with 1.4mM $\{W_{17}C_{20}\}$ in 0.1M H_2SO_4. Measurements were taken in air over a spectral range of 190-1000nm.

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.

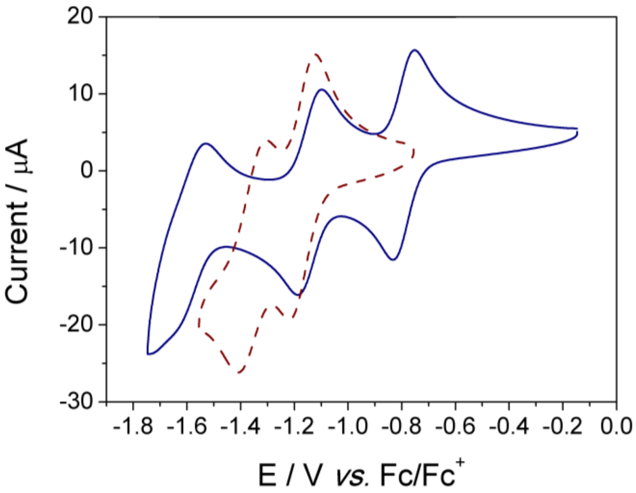

Figure S1 - A cyclic voltammogram of ***{P_2W_{18}}*** *(red) and* ***{$W_{17}C_{20}$}*** *(navy blue) (1.4 mM) in DMF with 0.1M TBA.PF_6 as the supporting electrolyte.*

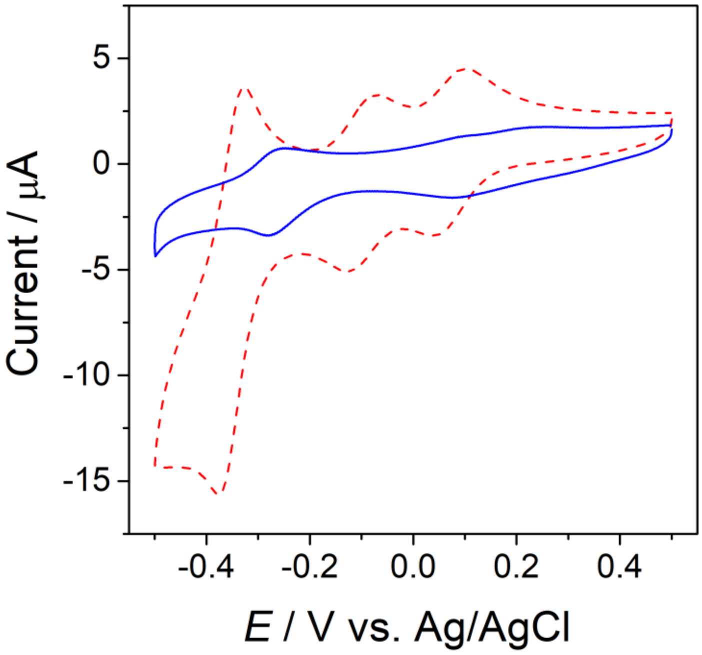

Figure S2 - Cyclic voltammogram of {$W_{17}C_{20}$} in 0.1 M H_2SO_4 (i.e. micellar form; blue line), and upon addition of 2 mL DMF (i.e. molecular form, red dashed line).

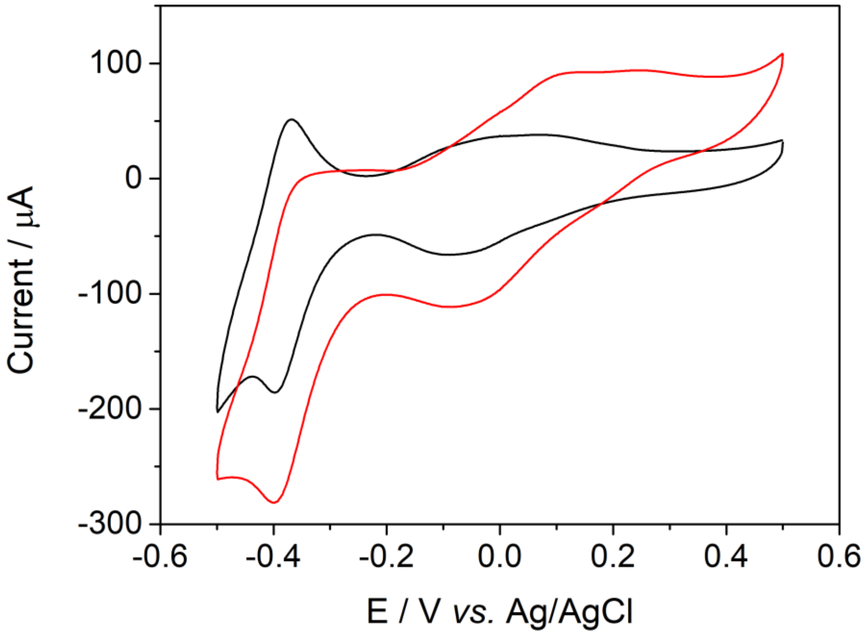

Figure S3 - Cyclic voltammogram of 1.4 mM ***{$W_{17}C_{20}$}****(red) and* ***{$W_{17}C_{20}$}*** *SAM (black) on GC square electrode in 0.1M H_2SO_4 supporting electrolyte. This modified electrode was used for surface analysis.*

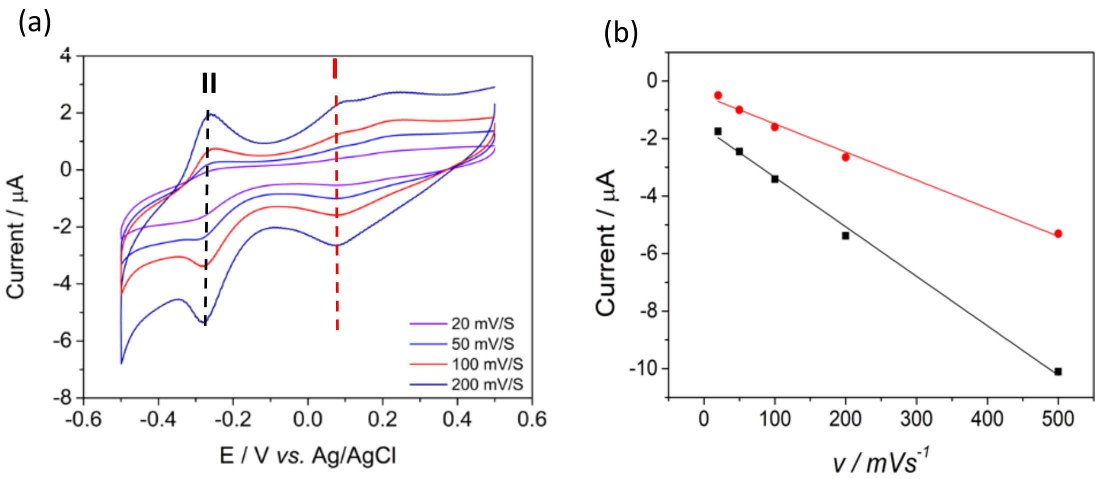

Figure S4 - (a) CV plot of {$W_{17}C_{20}$} at various scan rates(v) in 0.1M H_2SO_4; (b) a plot of the I_p vs v extrapolated from CVs in (a).

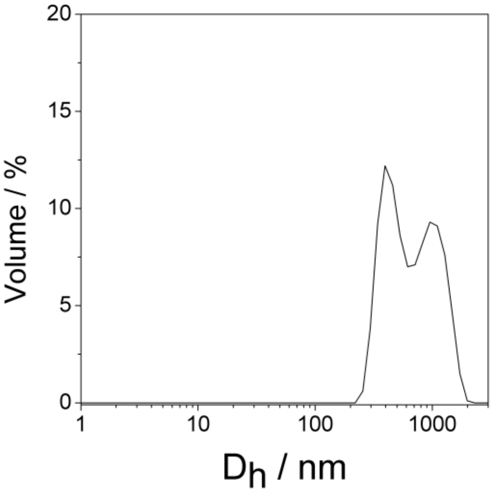

Figure S5 - DLS of {$W_{17}C_{20}$} micelle solution (1.4 mM) in 0.1 M H_2SO_4 + 2 ml DMF which displays no small micellar assemblies.

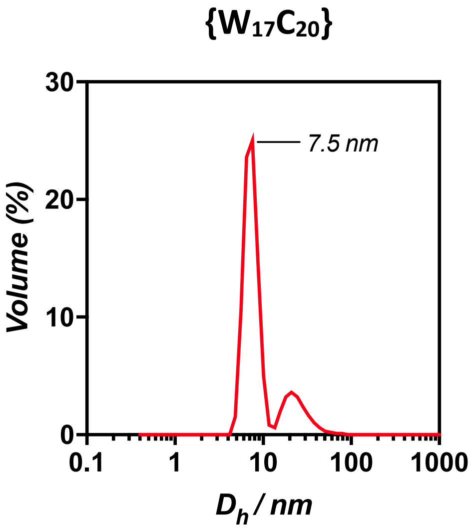

Figure S6 - Particle-size distribution analysis of {W17C20} (1.4 mM) in 0.1 M H2SO4.

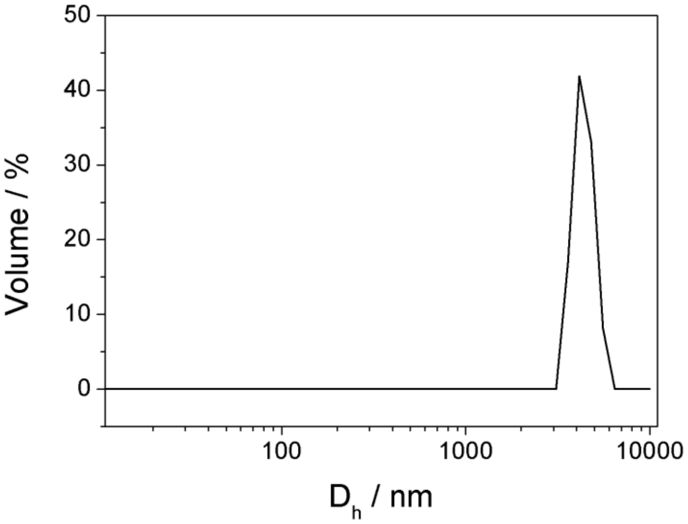

Figure S7 - DLS analysis of 1.4 mM ***{$W_{17}C_{20}$}*** *in DMF which indicates no small nanoaggregates in solution. (Note that this behaviour is representative of all* ***{$W_{17}C_n$}*** *species dissolved in neat DMF.*

Atomic force microscopy

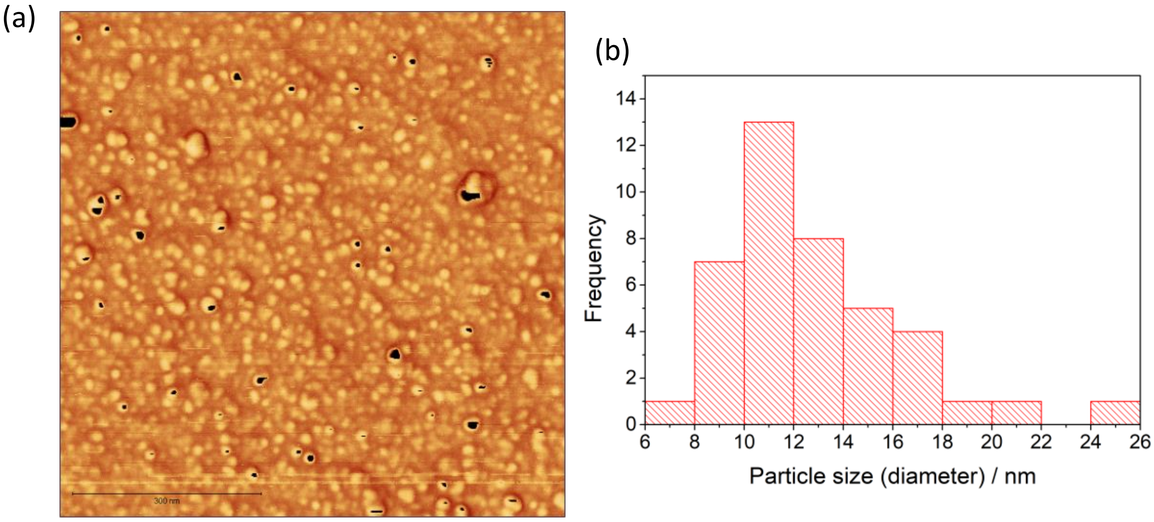

Figure S8 - (a) AFM phase image of micelles @ glassy carbon electrode and (b) histogram of particle size distribution in (a).

Theoretical monolayer reduction calculation

Surface area of electrode (d = 3 mm) = πr^2 = 7.069 x 10^{-6} m^2

Cross-sectional area of micelle (d = 7 nm) = πr^2 = 3.85 x 10^{-17} m^2

No. of micelles in a full theoretical monolayer = Area of electrode / area of micelle = 1.84 x 10^{11}

Surface area of micelle (d = 7 nm) = $4\pi r^2$ = 1.54 x 10^{-16}

Radius of POM = ((0.75 x 10^{-9}) + 1.041 x 10^{-9})/2 = 8.96 x 10^{-10}

Note: d = 1.041 nm was acquired from the Van der Waals space filling mode where the width of the cluster. We further accounted for K^+ intercalation by acquiring the average K^+---O= bind distance from a POM crystal structure (0.375 nm) and added 2x for charge balancing cations either side of the cluster.

Cross-sectional area of the POM = πr^2 = π (8.96 x 10^{-10})^2 = 2.5 x 10^{-18}

No. of POMs in a micelle (d = 7 nm) = Surface area of micelle /Cross-sectional area of the POM = 1.54 x 10^{-16} / 2.5 x 10^{-18} = 62 (61.6) POMs

No of POMs in a monolayer of micelles @ electrode = 62 x 1.84 x 10^{11} = 1.14 x 10^{13}

Moles of POM in a monolayer of micelles @ electrode = 1.14 x 10^{13} / 6.022 x 10^{23} = 1.864 x 10^{-11}

Moles of POM involved in reduction = 8 x 10^{-12}

POMs active in a full theoretical monolayer of micelles @ electrode = (8 x 10^{-12} / 1.86 x 10^{-11}) x 100 = 43%

SEM & TEM

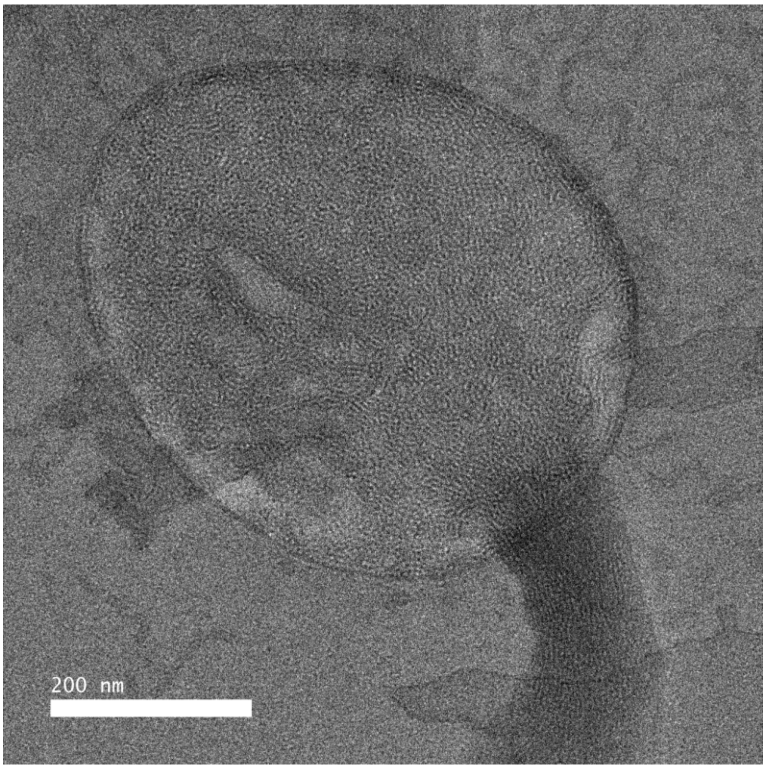

Figure S9 - TEM image of 1.4mM {$W_{17}C_{20}$} in 0.1 M aq H_2SO_4 dropcasted on GO supported TEM grid.

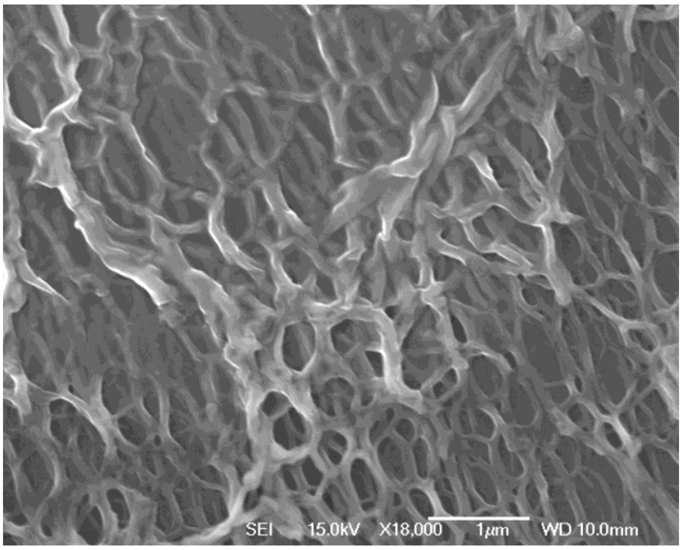

Figure S10 - SEM image of 1.4mM {$W_{17}C_{20}$} in 0.1 M aq H_2SO_4 dropcasted on HOPG. Deposition from H_2SO_4 leads to more defined and smaller fiber like structures.

Ellipsometry

The ellipsometry was carried out on an Accurion ep4 imaging ellipsometer. The ellipsometer was fitted with a 7X UV lens capable of making measurements between 190 and 1000nm. Initially an uncoated area of the electrode was imaged to obtain optical properties of the glassy carbon substrate. As the coating appeared to not be uniform the ellipsometry operated in rotating compensator ellipsometry (RCE) mode as this allows for fitting of a range of film thickness in a single measurement. Values for Delta and Psi were obtained over an area of 820 by 920 µm for wavelengths between 190 and 1000 nm in 10 nm steps.

The values for delta and psi were sent to Accurions in built modelling software. To fit the values of n and k a model was created (Figure S14). This model consisted of multiple Gaussian peaks centred at 4.1, 5.69 and 6.09 eV. This model was checked at multiple points of the sample to ensure its accuracy. To create the 2D map Accurions software used the signal at 230 nm and the created model to calculate the thickness in each area of the sample. To improve accuracy and fitting speed the pixels were averaged over a 3x3 area.

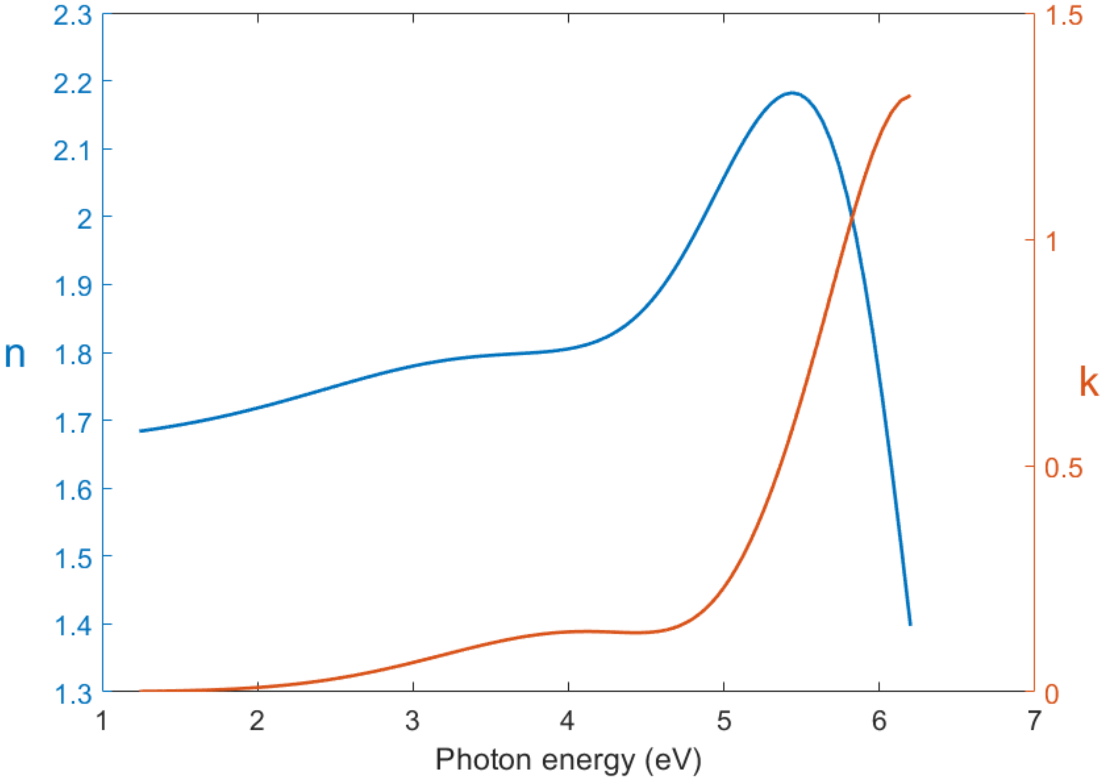

Figure S11- refractive index (n) and extinction coefficient (k) of {$W_{17}C_{20}$}.