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Supplementary information for

Complex-Decorated Surfactant-Encapsulated Clusters (CD-SECs) as novel multidynamic hybrid materials

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S1 Experimental methods

S1.1. Materials and methods

Scanning (SEM) electron microscopy characterizations were carried out by using a SEM FEI Quanta 250 FEG instrument with energy-dispersive X-ray (EDX) and FEI Tecnai F20 S/TEM equipped with EDX. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo STAR System TGA/DSC 2 set-up operating with a heating rate of 10 °C min^{-1} under flowing air. The Fourier transform infrared spectra (FT-IR) were recorded within the mid-IR range (400−4000 cm^{-1}) by using a Spectrum Two FT-IR spectrometer (Perkin Elmer) equipped with ATR Diamond. X-ray photoelectron spectroscopy (XPS) analyses were done by employing a Thermo Scientific KAlpha X-ray photoelectron spectrometer with a basic chamber pressure of ~10^{-9} mbar and an Al anode as the X-ray source (X-ray radiation of 1486 eV). Spot sizes of 400 µm were used and pass energies of 200.00 eV for wide energy scans, while for normal scans 10.00-20.00 eV were used. Organic elemental analysis (C, H, N) was done by following standard procedure using Thermo Scientific FLASH 2000 HT/IRMS Analyzers. Hydrodynamic radius analyses were executed using Malvern Zetasizer Nano S instrument, equipped with a 630 nm He-Ne laser, with the detector collecting the backscattering signal (173° geometry). X-ray powder diffraction (XRD) was performed on a Bruker ASX D8 Advanced equipped with Cu anode with Kα radiation (λ = 1.5418 Å). Diffraction patterns were collected at room temperature in the scattered angular range between 6° and 60° with an angular resolution of 0.02° per step and a typical counting time 4 of 10 s per step.^{1}H NMR, ^{13}C NMR, VT and NMR spectra were recorded at 300 MHz for ^{1}H and 75 MHz for ^{13}C (Bruker Fourier 300), or 600 MHz for ^{1}H and 150 MHz for ^{13}C (Bruker Avance III) in deuterated solvents. Chemical shifts are reported in ppm relative to the residual solvent peak. Data are reported as follows: chemical shift (δ), multiplicity (s for singlet, d for doublet, t for triplet, m for multiplet, brs for broad peaks), coupling constant (J in Hertz), and integration. DOSY NMR spectroscopy was carried out on Bruker Avance III HD 700 MHz.

S2 Synthetic procedures and characterization

All chemicals and solvents were purchased from commercial sources (mainly Sigma-Aldrich) and used without further purification.

S2.1. Preparation of Wells-Dawson $K_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ POM

$K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot14H_2O$ was prepared according to the Finke method [2] and its purity was confirmed by using single crystal X-ray diffraction, elementary analysis, FT-IR and DLS.

Expected formula: $K_6[P_2W_{18}O_{62}]\cdot14H_2O$

Please note that to confirm structure of POM we recrystallized it by performing an alkaline cation exchange (here from potassium to sodium). For further reactions the sodium salt was used: $Na_6[P_2W_{18}O_{62}]\cdot14H_2O$ = $[P_2W_{18}]$

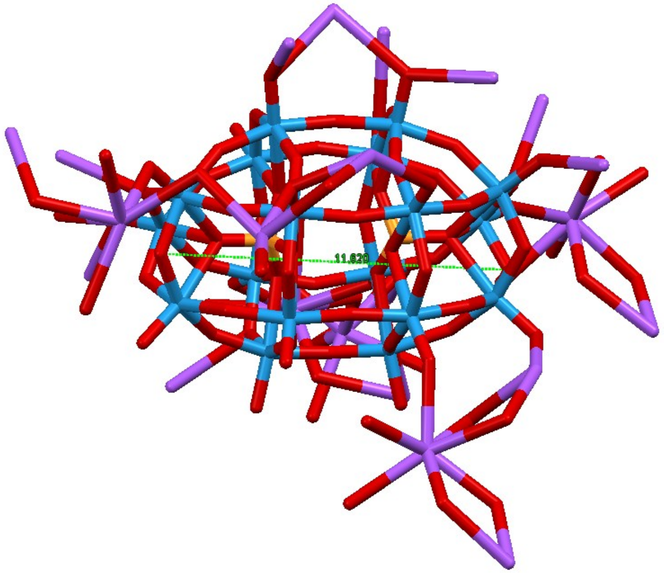


Fig. S1 Crystal structure of Wells-Dawson [$\mathbf{P_2W_{18}}$]

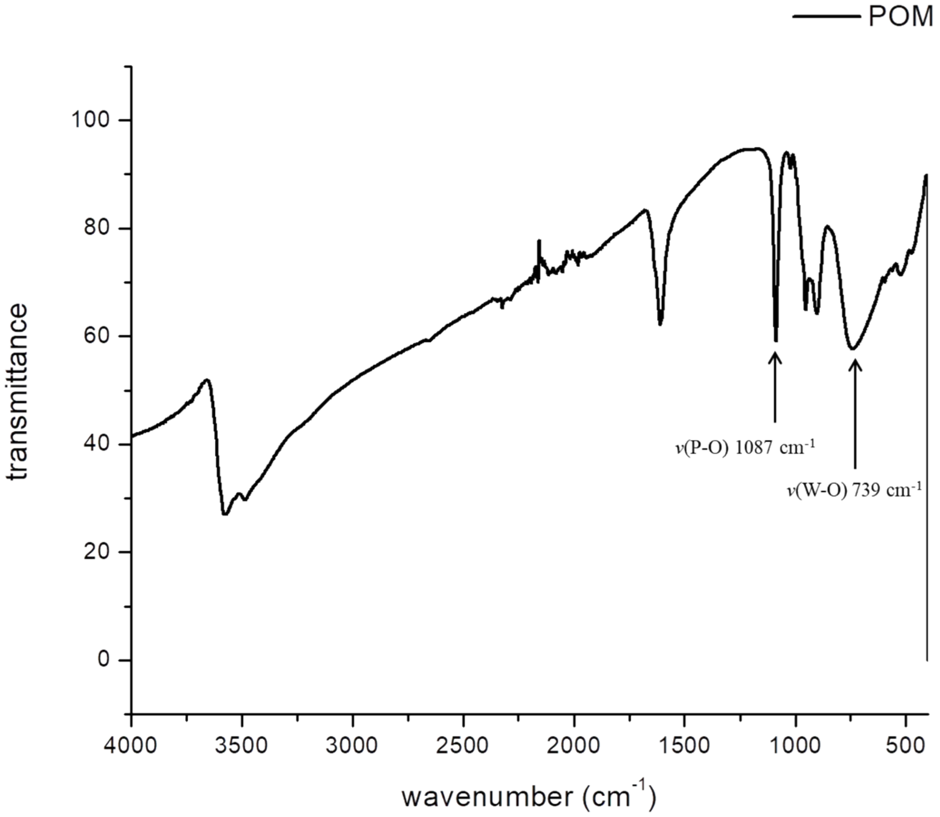


Fig. S2 IR spectrum of Wells-Dawson [$\mathbf{P_2W_{18}}$]

In the IR spectrum one can observe analytical P-O (1087 cm^{-1}) and W-O (739 cm^{-1}) stretching vibrations.

Dynamic Light Scattering (DLS)

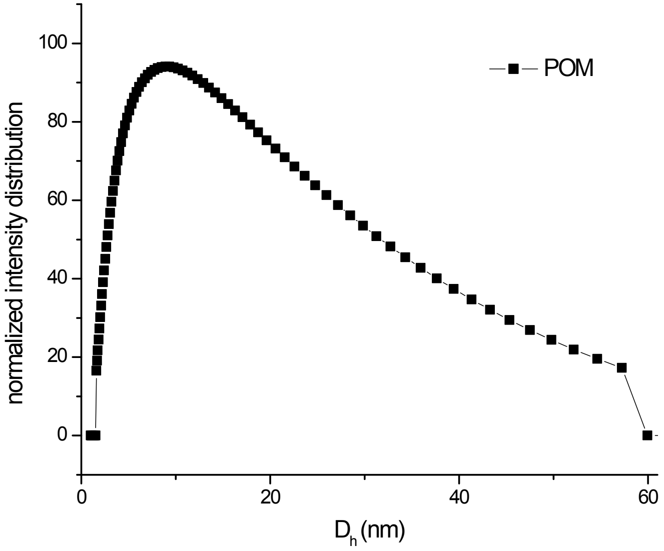


Fig. S3 Dynamic light scattering (DLS) diagram of **[P_2W_{18}]**.

Dynamic light scattering (DLS) measurement shows that **[P_2W_{18}]** species in DMSO as solvent and concentration of $2{\cdot}10^{-4}$ M self-organize into spherical assemblies with a maximum hydrodynamic distribution (D_h) concentrated at around 10 nm. The distribution of measurements is up to the value around 60 nm what one can observed that on the SEM images there are different assemblies sizes.

Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS)

1. Solid state:

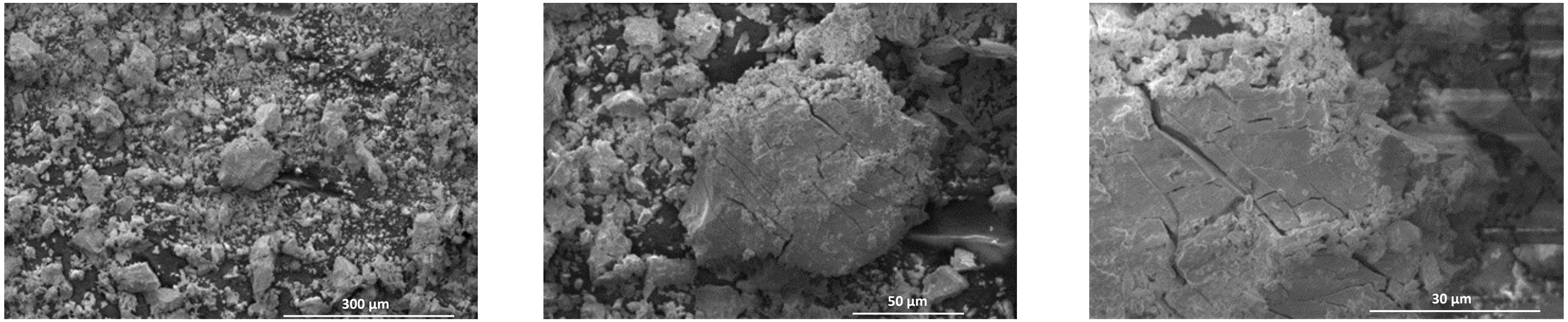


Fig. S4 Scanning electron microscopy (SEM) images of solid **[P_2W_{18}]** assemblies.

2. Drop-casting:

a) dissolved in DMSO and evaporated

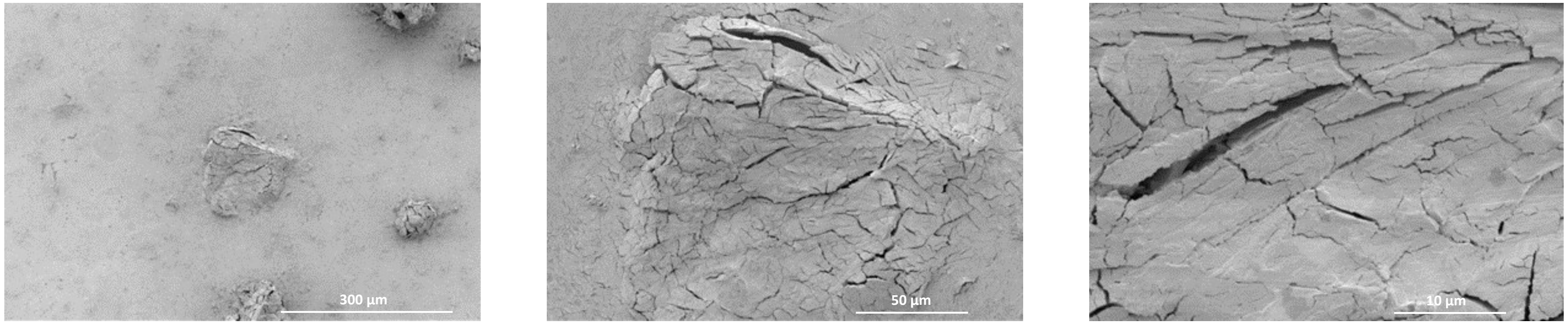


Fig. S5 Scanning electron microscopy (SEM) images of evaporated **[P_2W_{18}]** assemblies.

b) dissolved in DMSO and heated

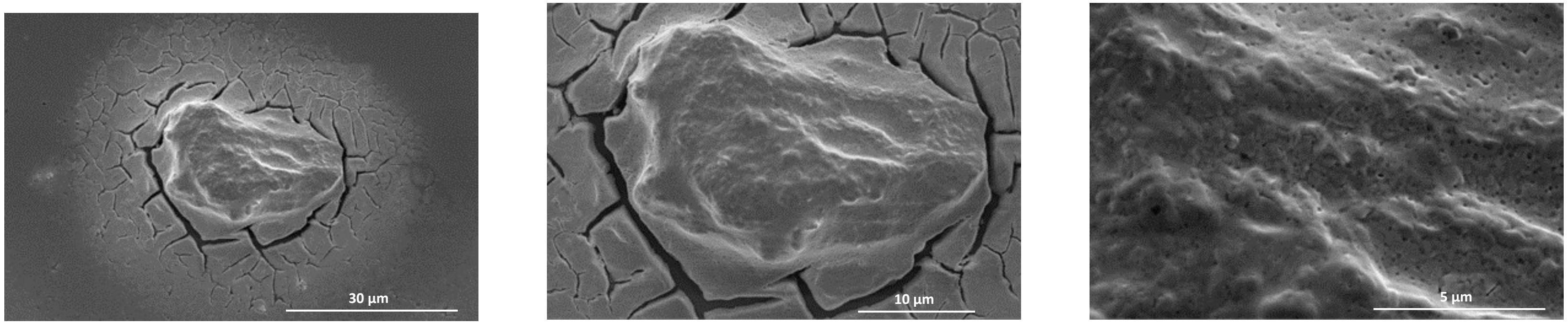
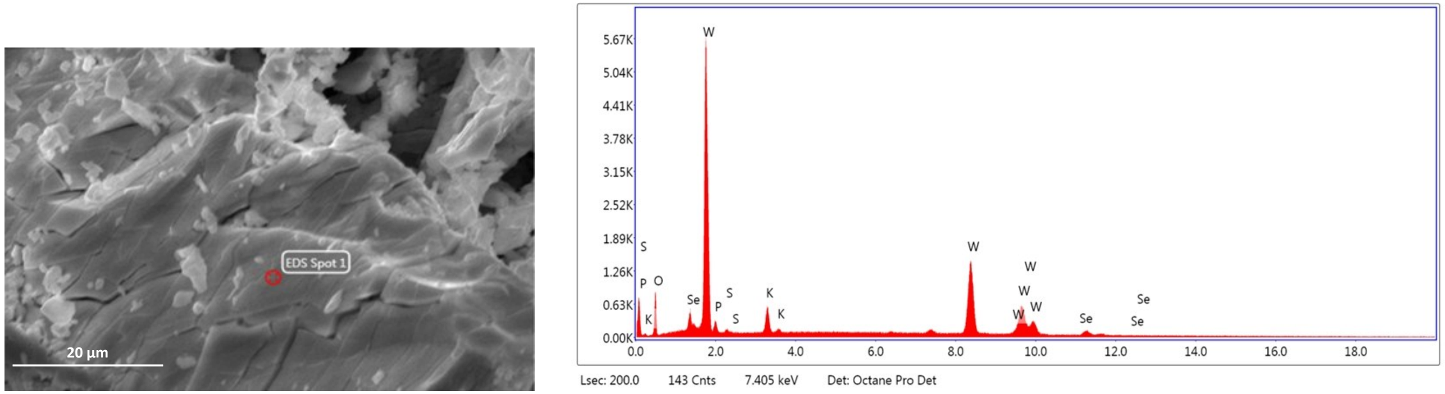
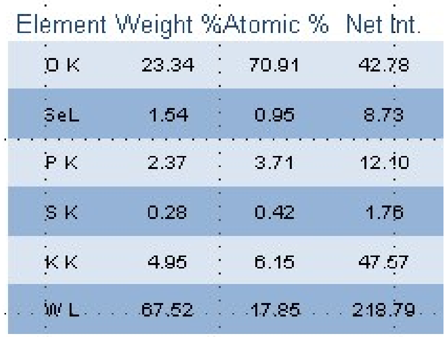


Fig. S6 Scanning electron microscopy (SEM) images of heated **[P_2W_{18}]** assemblies.

3. EDS





Element	Weight %	Atomic %	Net Int.
O K	23.34	70.91	42.78
SeL	1.54	0.95	8.73
P K	2.37	3.71	12.10
S K	0.28	0.42	1.76
K K	4.95	6.15	47.57
W L	67.52	17.85	218.79

Fig. S7 Scanning electron microscopy (SEM) image of solid **[P_2W_{18}]** POM and its X-ray energy dispersion spectrum.

At SEM image one can observe high level of crystallinity of **[P_2W_{18}]** POM, which possesses 3D porous and a highly homogenous architecture in solid state. In turn, when sample was dissolved in DMSO and evaporated one can note another type of morphology – sample are no longer crystalline. In case of heated samples of POM there are cavities in whole surface. Energy Dispersive Spectroscopy (EDS) shows that anticipated elements like tungsten, phosphorus and oxygen are present in the studied sample.

S2.2. Preparation of ligand L, [ZnLCl$_2$] and [ZnL$_2$(ClO$_4$)$_2$] complexes

Compounds were synthesized as reported by us previously.[3]

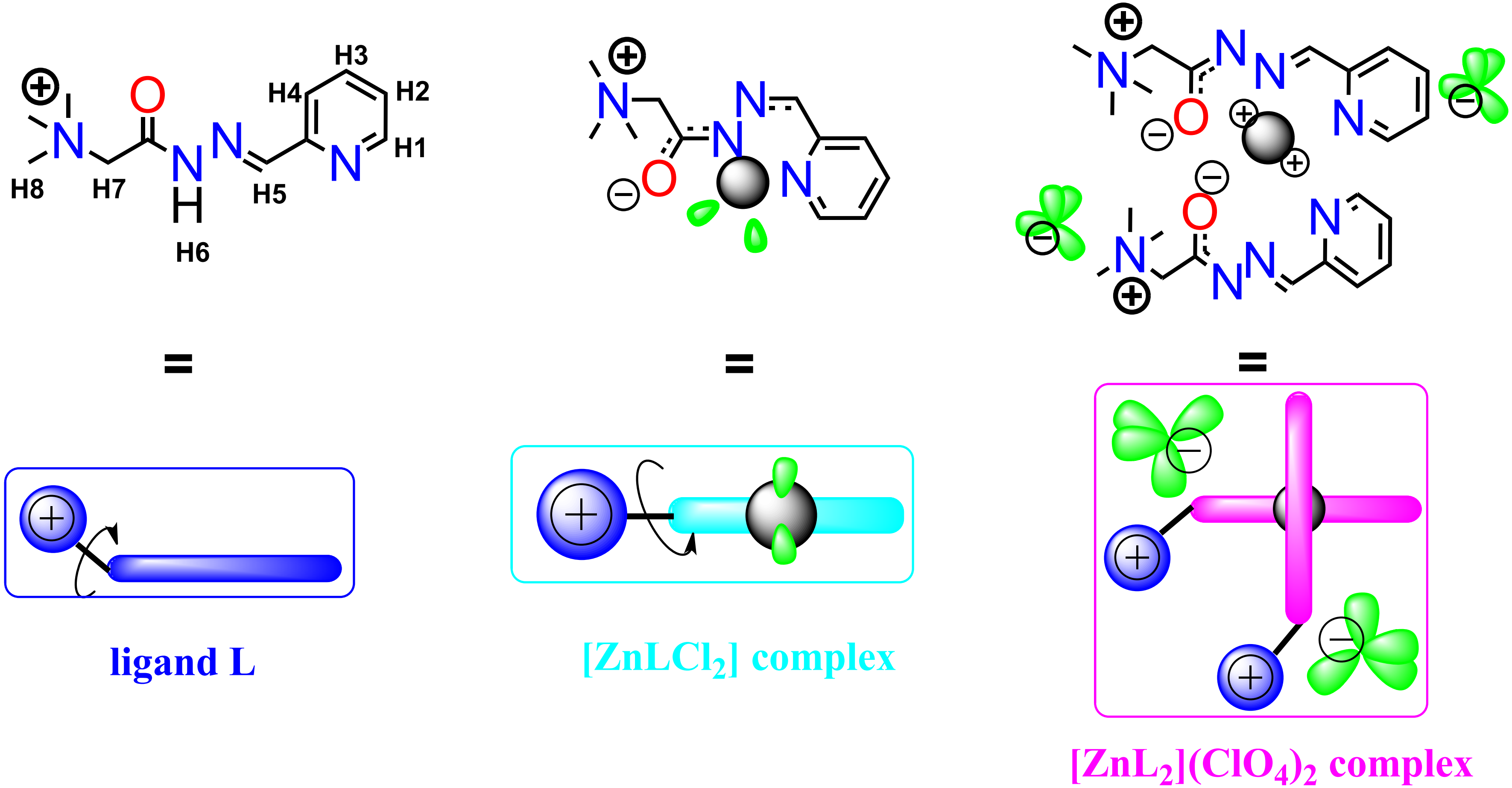


Fig. S8 Schematic representation of **L**, [Zn**L**Cl$_2$] and [Zn**L**$_2$](ClO$_4$)$_2$ structures, respectively.

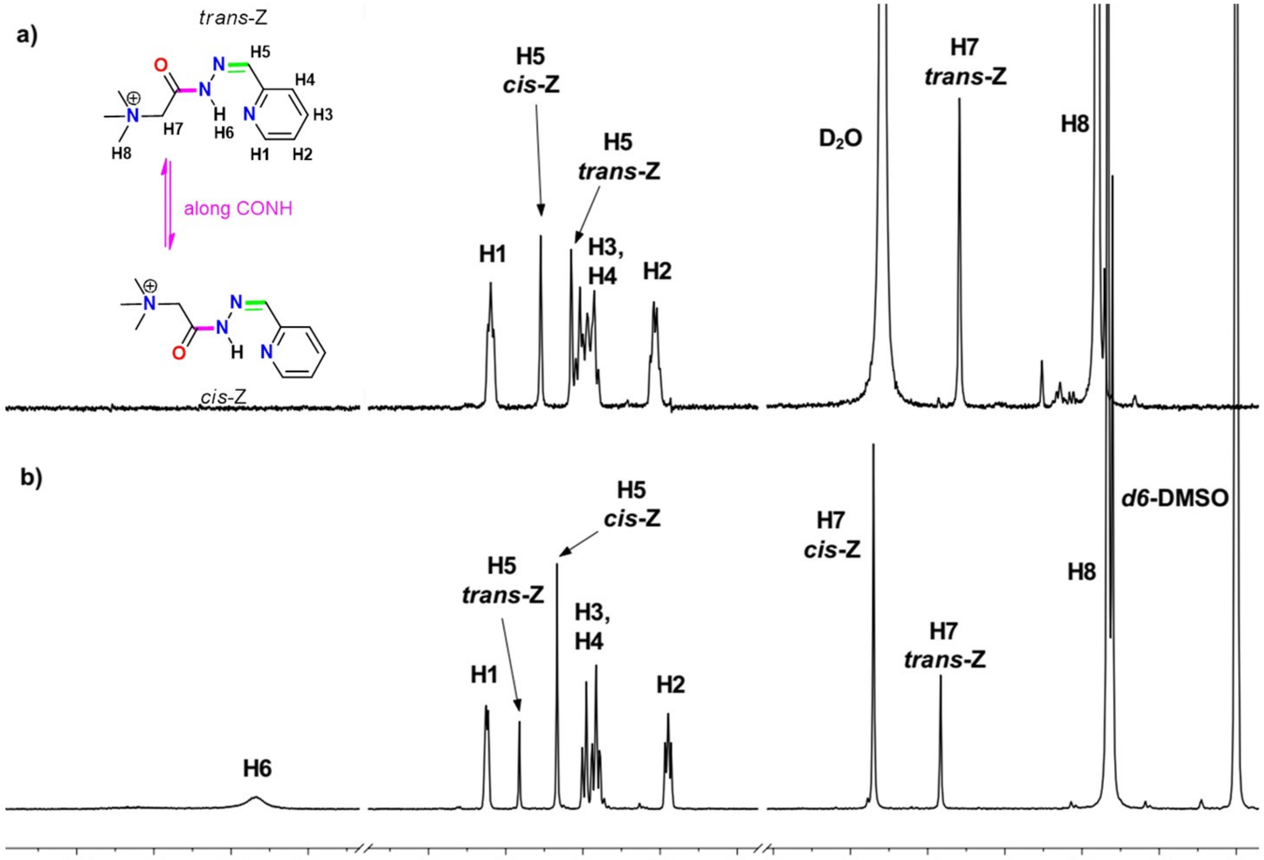


Fig. S9 ^1H NMR spectrum (300 MHz) of possible isomers *trans*-Z and *cis*-Z for ligand **L** in a) D_2O and b) *d6*-DMSO

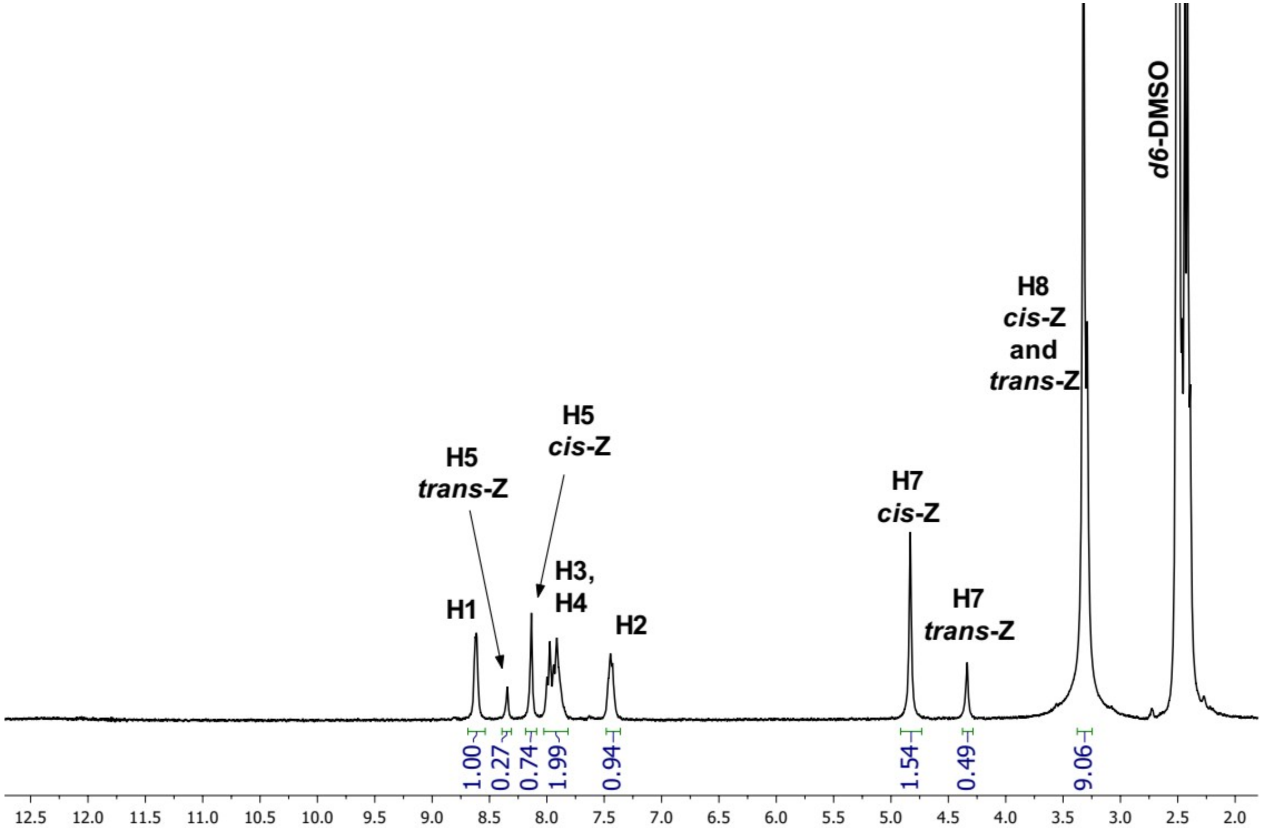


Fig. S10 ^{1}H NMR spectrum (300 MHz, DMSO-*d6*) of ligand **L**+ Et_3N

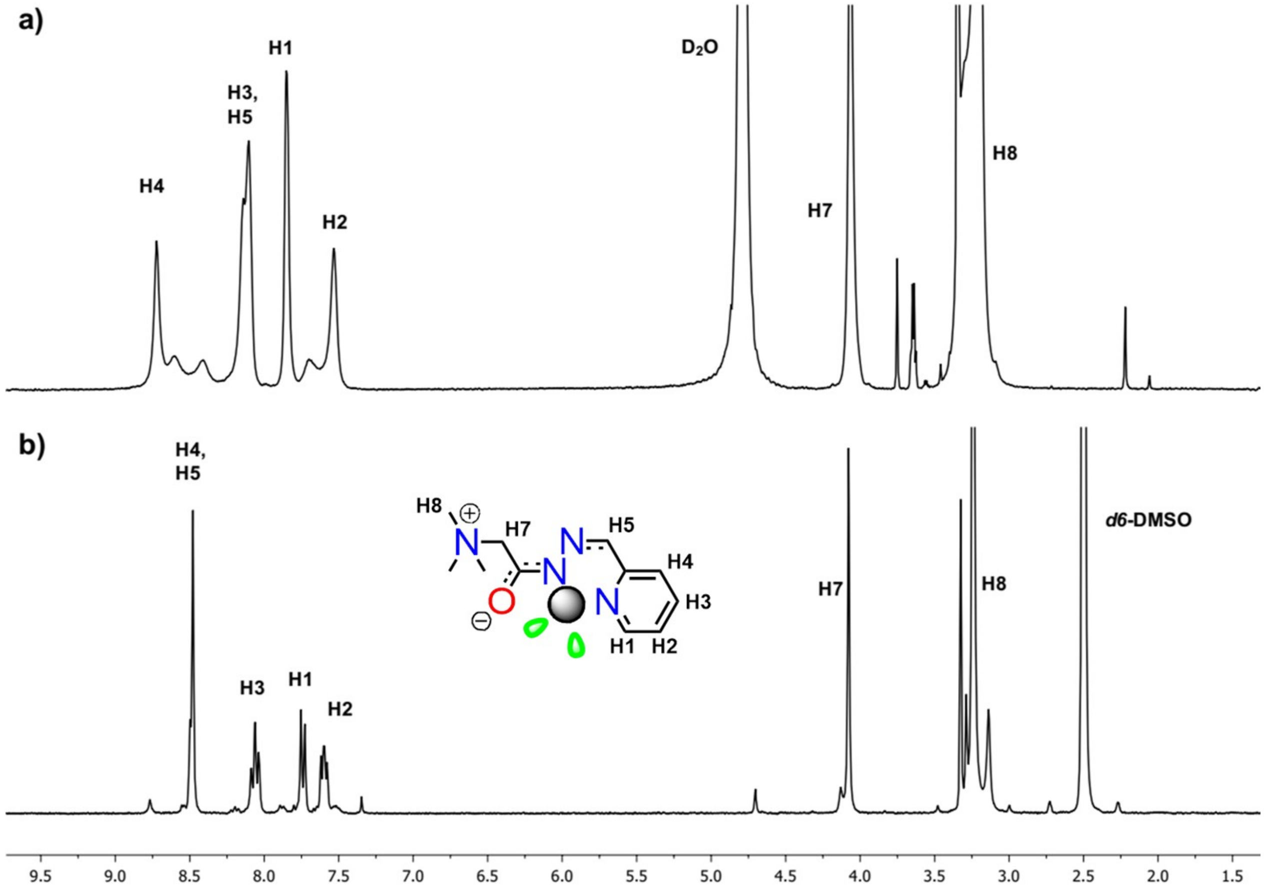


Fig. S11 ^{1}H NMR spectrum (300 MHz) of complex [Zn**L**Cl$_2$] in a) D$_2$O and b) *d6*-DMSO

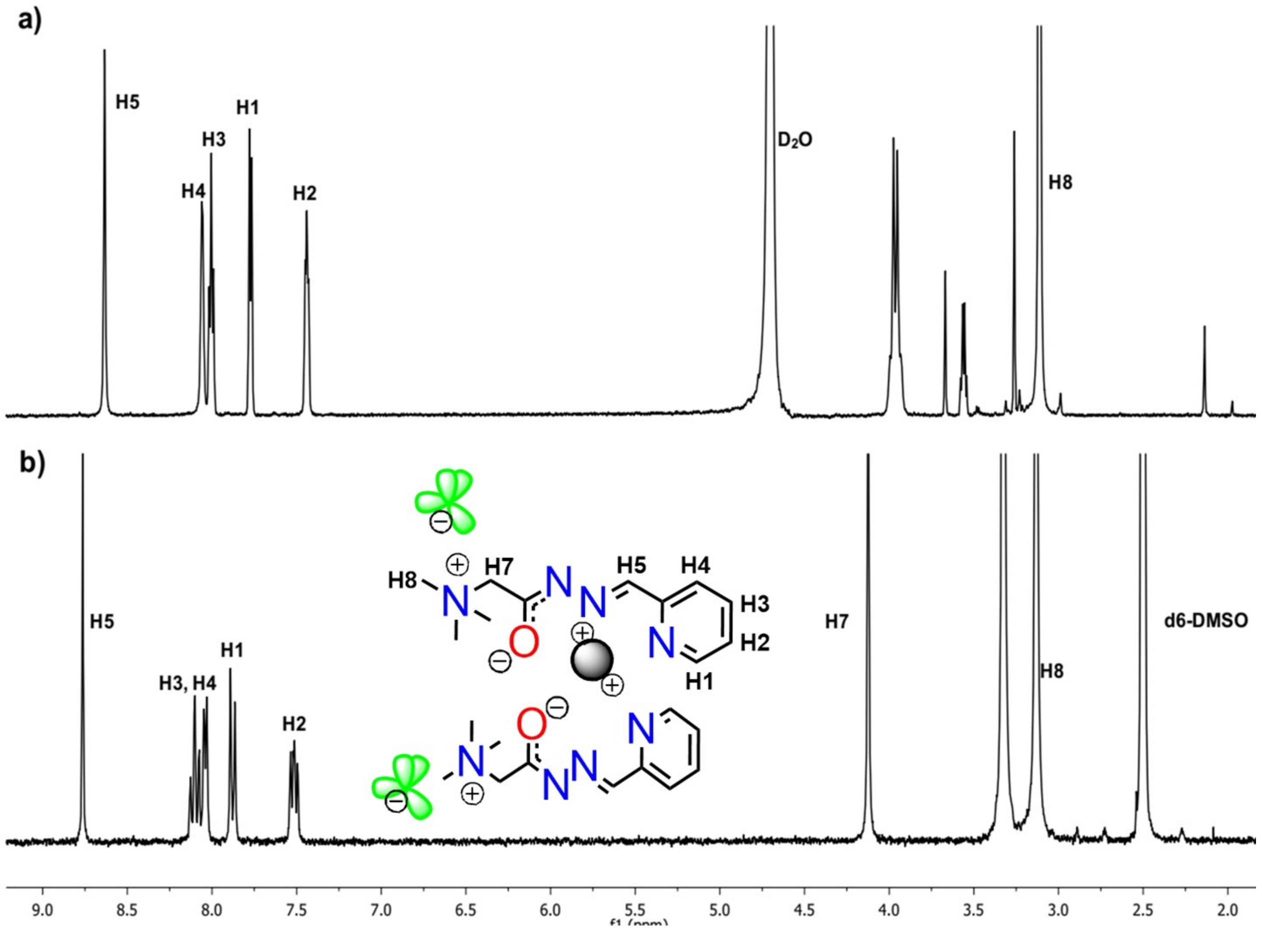


Fig. S12 ^{1}H NMR spectrum (300 MHz) of complex [Zn**L₂**(ClO₄)₂] in a) D₂O and b) *d6*-DMSO

S2.3. Preparation of hybrids H1-H3

Three families of hybrid materials **H1**-**H3** are envisaged (**H1** - SEC and two CD-SECs **H2**, **H3**) that can be possibly formed *via* seven different routes (**routes A-C** – direct synthesis {POM+**L**/[Zn**L**Cl$_2$]/[Zn**L**$_2$](ClO$_4$)$_2$}; **routes D,E** – titration of **H1** with Zn(II) salt {**H1**+ZnCl$_2$/Zn(ClO$_4$)$_2$}; **routes F**,**G** – one-pot synthesis POM+**L**+ZnCl$_2$/Zn(ClO$_4$)$_2$). We also compare the effect of *in situ* formation of target material (**Hx$_{in\_situ}$**) vs its isolation (**Hx$_{isol}$**) on its characteristics, followed by insight into variables such as solvent or pH.

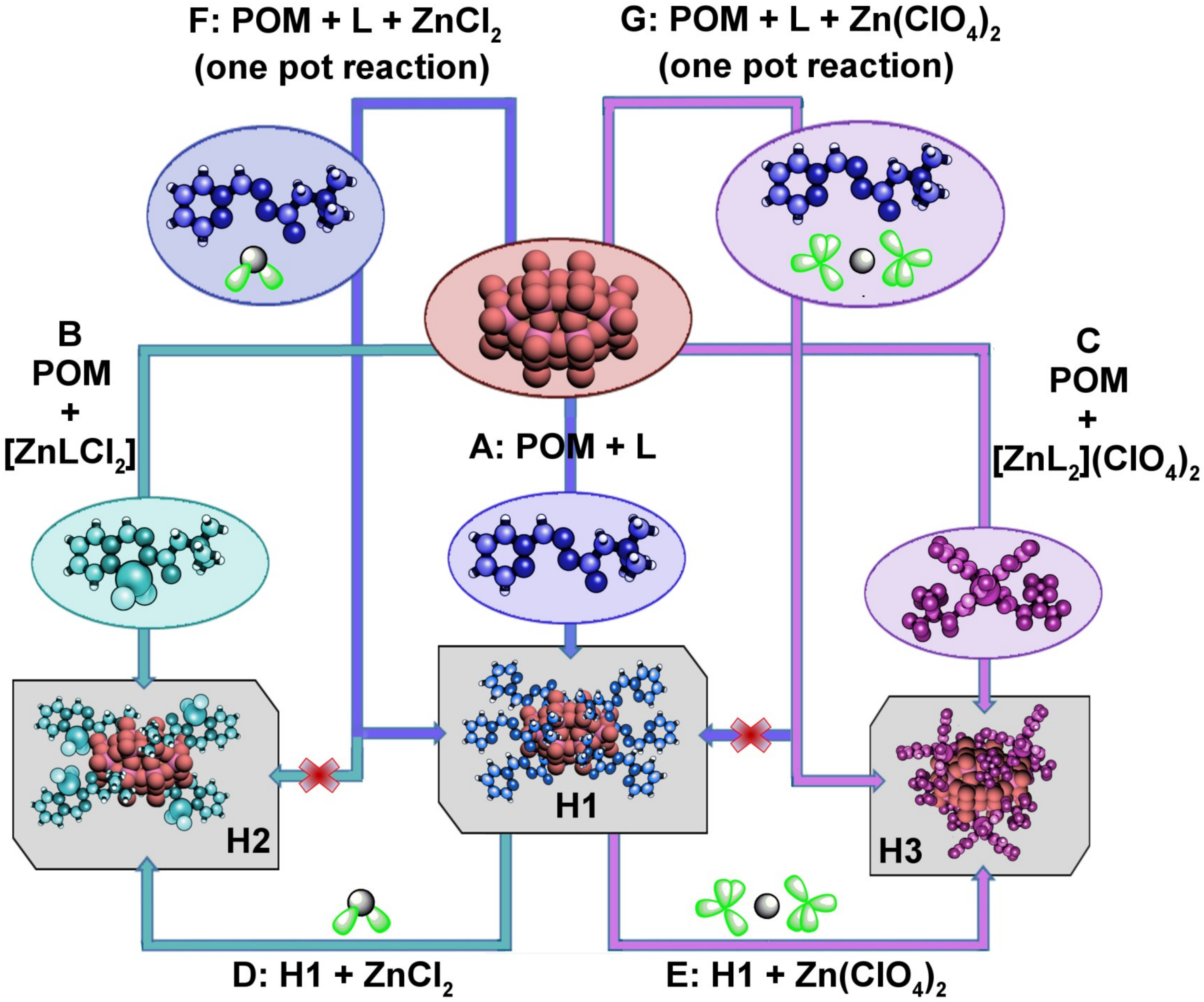


Fig. S13 Summary of work including different synthetic pathways

S2.3.1. Route A (POM + ligand L) - Synthesis of hybrid $H1_{isol}$ – SEC – $[P_2W_{18}\text{-}(L)_6]$

$Na_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ (126.4 mg; 26·µM) was dissolved in 15 ml of mili-Q water what resulted in a clear yellow solution. Next, clear colourless solution of ligand **L** (40 mg, 0.16 mM) was prepared in 4 ml of mili-Q water and added to the first one to give light yellow, cloudy solution. The mixture was stirred magnetically at room temperature for 48 h to give blue coloured solution and monitored by changes in pH (from 5.63 for the sole POM to 7.81 for the hybrid material). The final product was centrifuged (3 series of 10 minutes at 4000 rpm), what was followed by washing with water in between the cycles. Obtained product was lyophilized to give blue solid state compound. Yield: 117.4 mg, 70.72% based on ligand **L**. ^1H NMR (600 MHz, *d6*-DMSO) δ=12.18 (s, 0.70H, **H6** *cis*-Z),12.16 (s, 0.30H, **H6** *trans*-Z), 8.64-8.64 (m, 1H, **H1**), 8.22 (s, 0.30H, **H5** *trans*-Z), 8.09 (s, 0.70H, **H5** *cis*-Z), 8.02-8.01 (d,J=7.75, 1H, **H3**),7.98-7.95 (m, 1H, **H4**), 7.49 – 7.47 (m, 1H, **H2**), 4.82 (s, 1.4H, **H7** *cis*-Z), 4.28 (s, 0.6H, **H7** *trans*-Z), 3.34 – 3.32 (m, 9H, **H8**)

Elementary analysis

Anal. calc. for H1 (M = 6113.42): C: 12.97, H: 1.81, N: 5.50%; found: C: 12.93, H: 1.94, N: 5.45%.

Expected formula: $Na_6(C_{11}H_{17}ClN_4O)_6[P_2W_{18}O_{62}] \cdot 4H_2O = [P_2W_{18}\text{-}(L)_6]$

IR

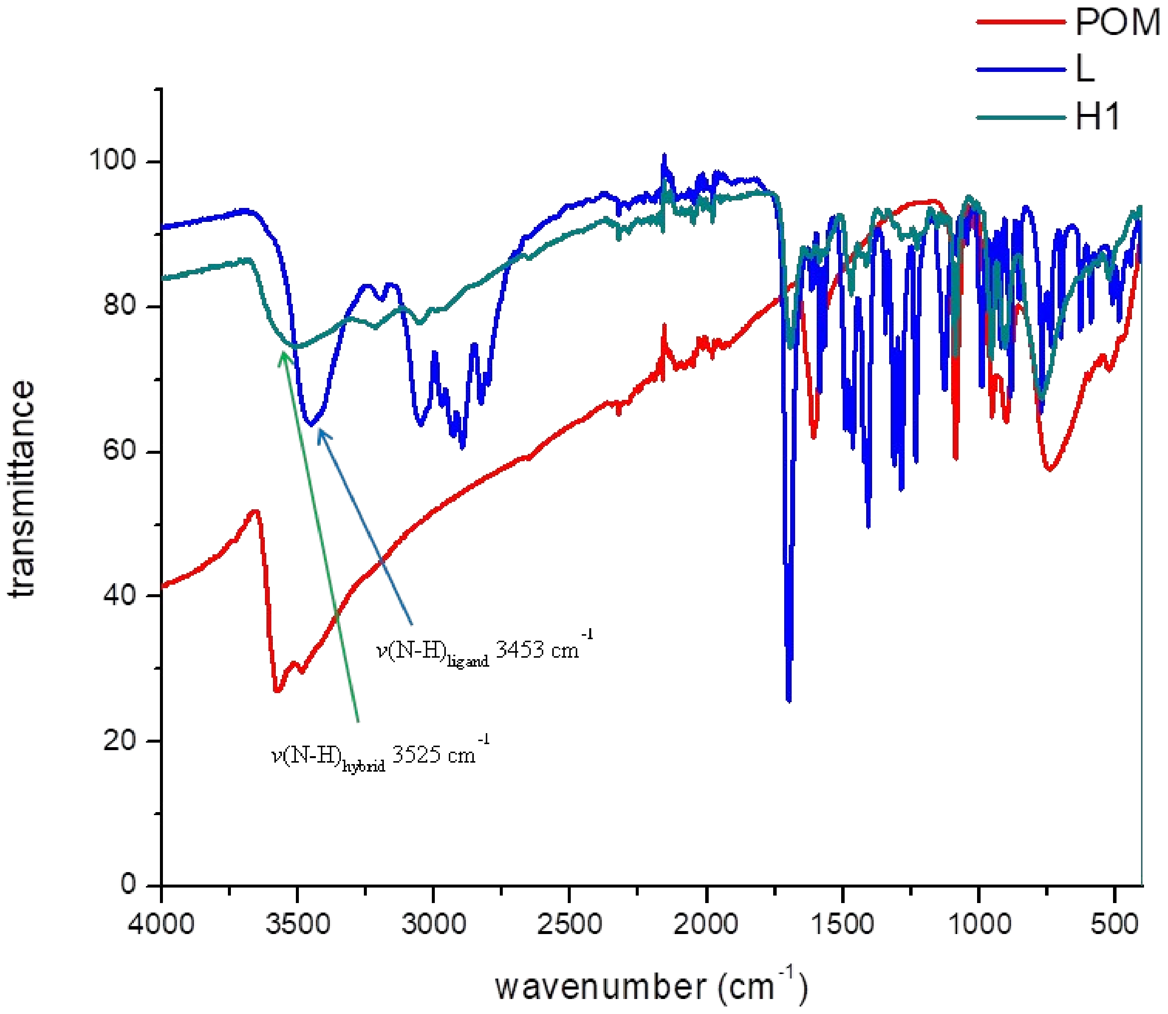


Fig. S14 Superimposed IR spectra of **POM**, **L** and hybrid **H1** in the wavenumber range from 4000 to 500 cm^{-1}

In the IR spectrum one can observe wavenumbers and peaks from N-H in ligand (3453 cm^{-1}) and occurring in hybrid H1 (3525 cm^{-1}).

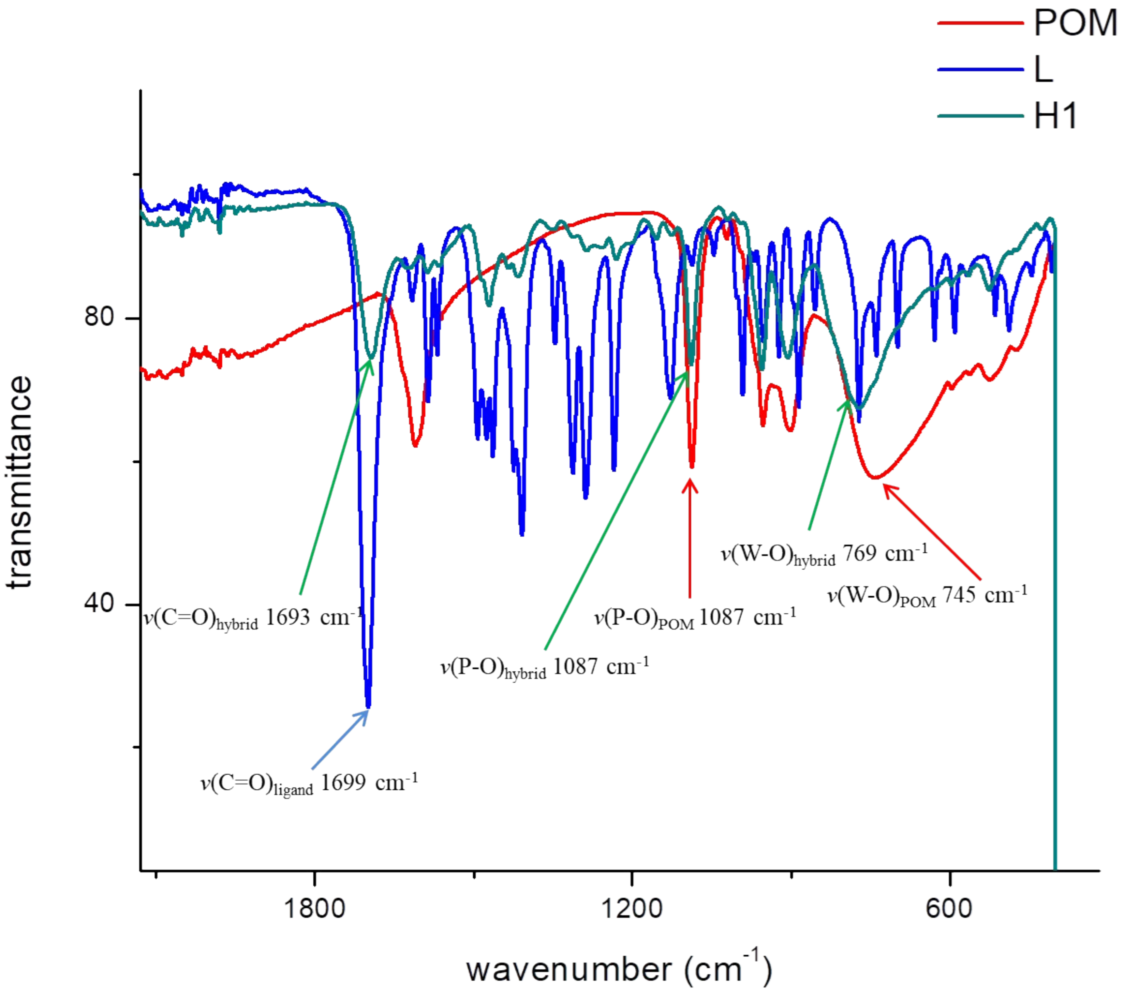


Fig. S15 Superimposed IR spectra of **POM**, **L** and hybrid H1 in the **H1**wavenumber range from 2100 to 300 cm^{-1}

In the IR spectrum one can observe wavenumbers and peaks from C=O are in wavenumber 1699 cm^{-1} and 1693 cm^{-1} respectively from ligand and hybrid. In turn, vibrations form P-O are in 1087 cm^{-1} for POM and hybrid what confirms stability of the Well-Dawson POM. Peak from W-O in POM is in 745 cm^{-1} and in 769 cm^{-1} from hybrid, what is a confirmation of creation of hybrid.

TGA (thermogravimetric analysis)

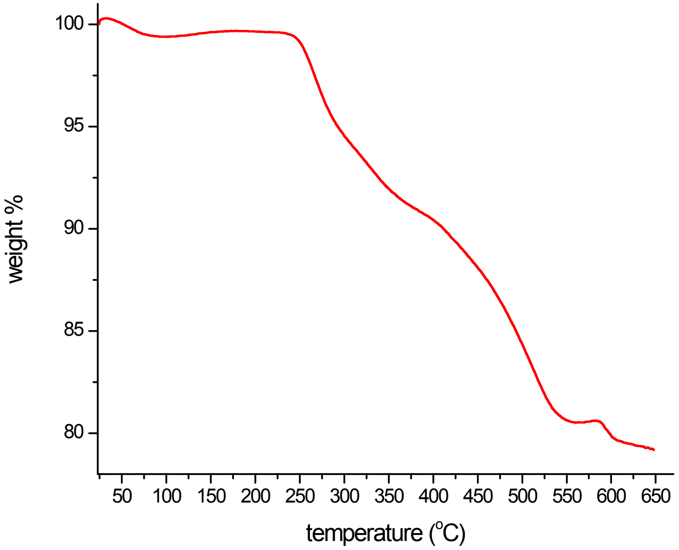


Fig. S16 TGA diagrams of **H1 [P_2W_{18}-(L)$_6$]**

In TGA analysis we observe that weight of the sample decreases in a two-step manner. First step, around 100°C, is ascribed to water molecules and the second one can be assigned to the gradual decomposition of organic ligand **L**. Difference between starting and ending value is around 20% what can be ascribed to the proposed formulae $Na_6(C_{11}H_{17}ClN_4O)_6[P_2W_{18}O_{62}] \cdot 4H_2O$ = [P_2W_{18}-(L)$_6$], where 6 hydrazone ligands are organized around the polyoxometalate via electrostatic interactions.

Dynamic Light Scattering (DLS)

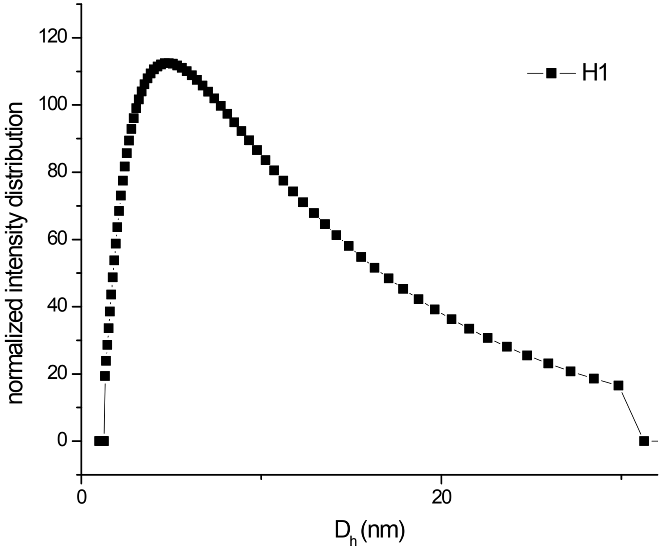


Fig. S17 Dynamic light scattering (DLS) diagram of **H1** **[P_2W_{18}-(L)$_6$]**

Dynamic light scattering (DLS) measurement shows that **[P_2W_{18}-(L)$_6$]** species, in DMSO as solvent and concentration of $2 \cdot 10^{-4}$ M appear as individual molecules with a maximum hydrodynamic distribution (D_h) concentrated around 5 nm, which corresponds well with the other characterization data. The distribution of measurements is up to the value around 30 nm. Moreover, stable **[P_2W_{18}-(L)$_6$]** assemblies with spherical shapes of various sizes are obtained by dropping the solution of assemblies on the silicon surface (see below - Fig. S19).

Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) and EDAX

1. Solid state:

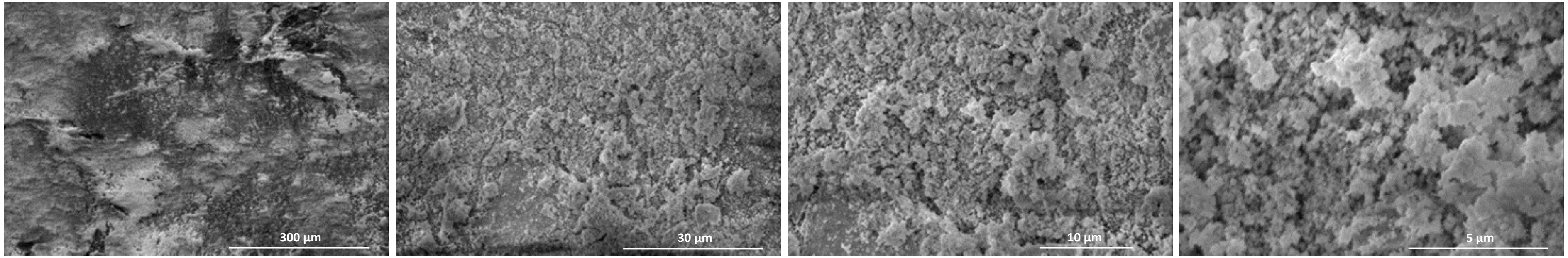


Fig. S18 Scanning electron microscopy (SEM) images of solid **H1 [P_2W_{18}-$(L)_6$]** assemblies.

2. Drop-casting:

a) dissolved in DMSO and evaporated

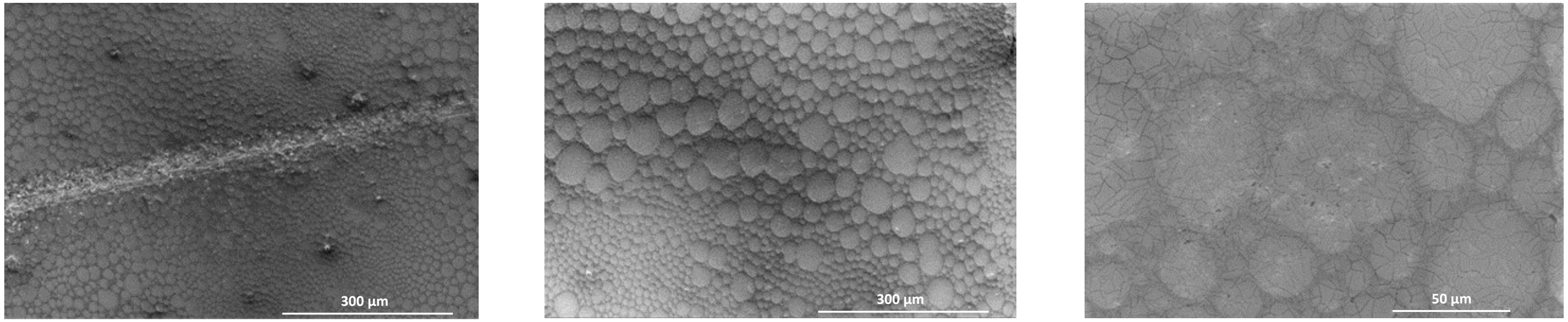


Fig. S19 Scanning electron microscopy (SEM) images of evaporated **H1 [P_2W_{18}-$(L)_6$]** assemblies.

b) dissolved in DMSO and heated

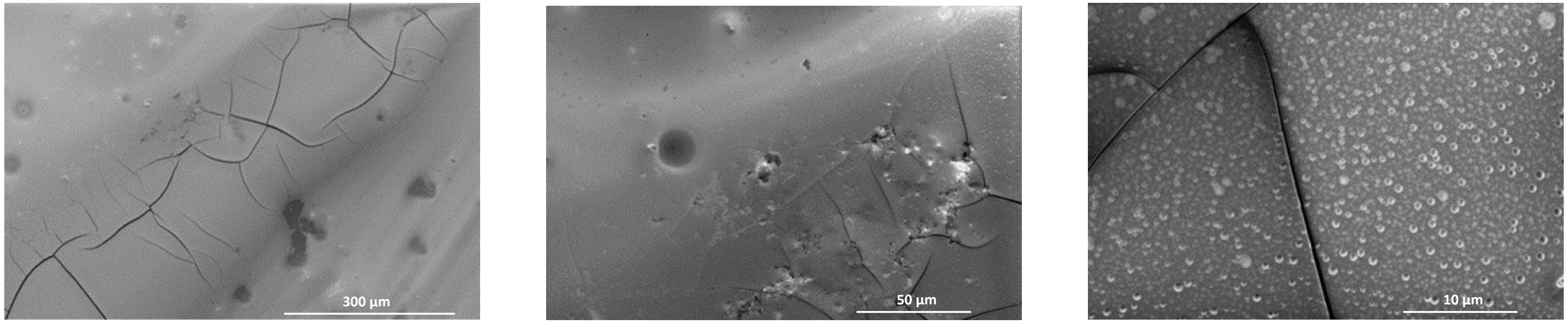
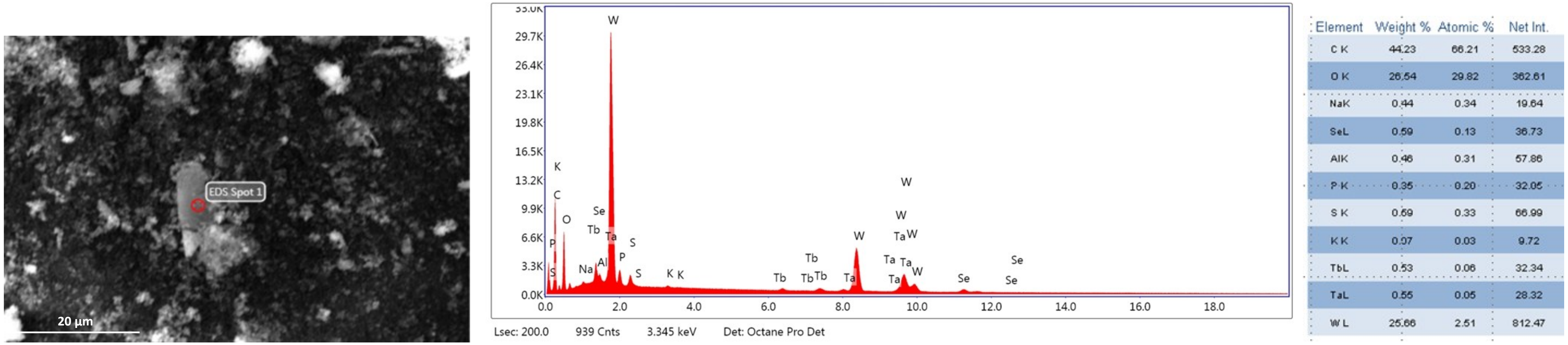


Fig. S20 Scanning electron microscopy (SEM) images of heated **H1 [P_2W_{18}-(L)$_6$]** assemblies.

3. EDS



Element	Weight %	Atomic %	Net Int.
C K	44.23	66.21	533.28
O K	26.54	29.82	362.61
NaK	0.44	0.34	19.64
SeL	0.59	0.13	36.73
AlK	0.46	0.31	57.86
P K	0.35	0.20	32.05
S K	0.69	0.33	66.99
K K	0.07	0.03	9.72
TbL	0.53	0.06	32.34
TaL	0.55	0.05	28.32
W L	25.66	2.51	812.47

Fig. S21 Scanning electron microscopy (SEM) image of solid **H1 [P_2W_{18}-(L)$_6$]** and its X-ray energy dispersion spectrum.

4. EDAX

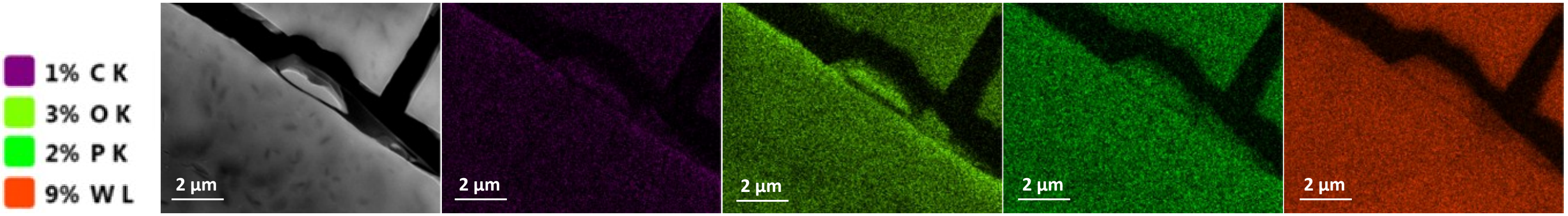


Fig. S22 EDAX analysis of solid **H1** in DMSO.

At SEM image one can observe layered surface of hybrid **$[P_2W_{18}\text{-}(L)_6]$** with aggregation in solid state. In turn, when sample was dissolved in DMSO and evaporated one can note another type of morphology – sample are orientated in some kind of spherical rings. In case of heated samples of POM there are cavities in whole surface. Energy Dispersive Spectroscopy (EDS) shows that anticipated elements like tungsten, phosphorus oxygen and carbon are present in the studied sample.

NMR spectroscopic characterization of $H1_{isol}$

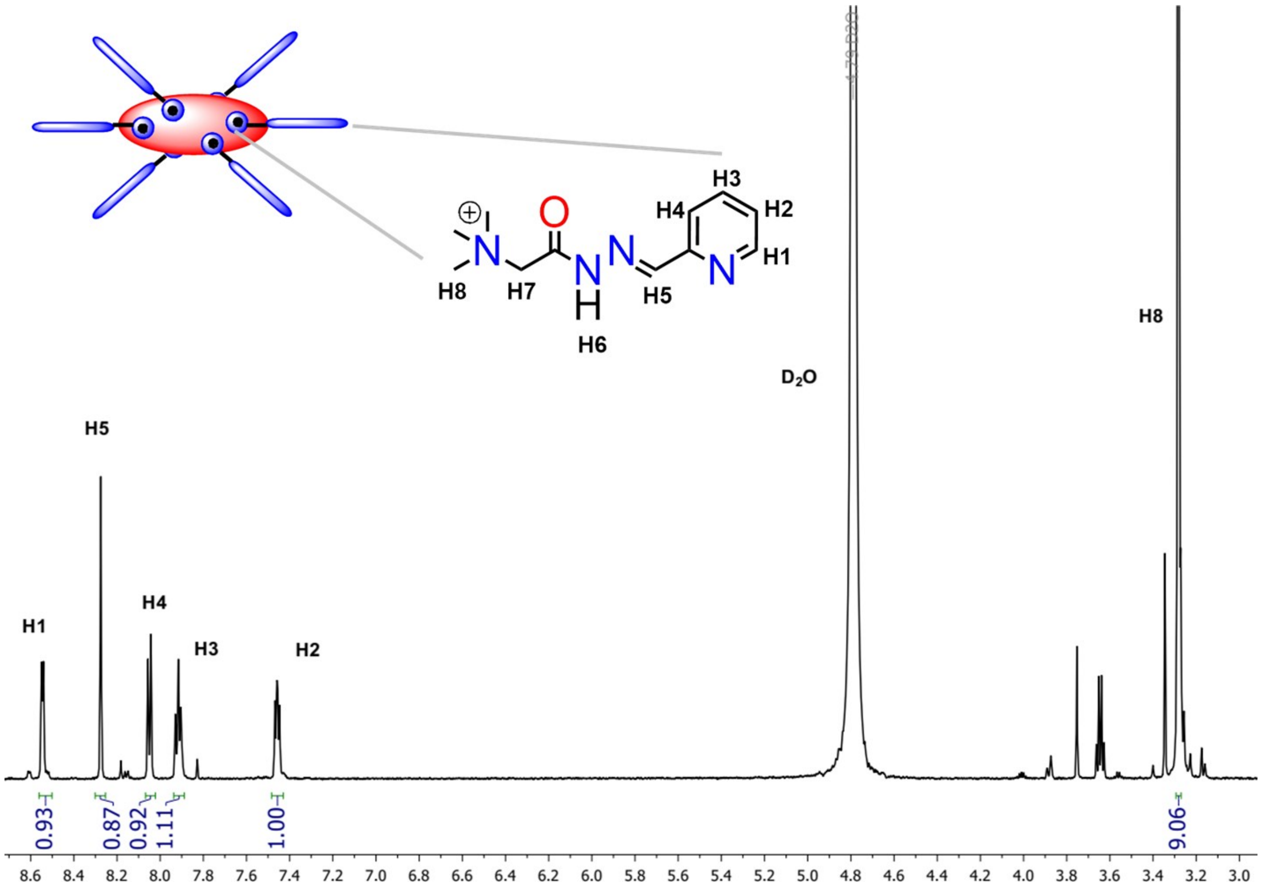


Fig. S23 ^{1}H NMR spectrum (600 MHz, D_2O) of $\mathbf{H1_{isol}}$

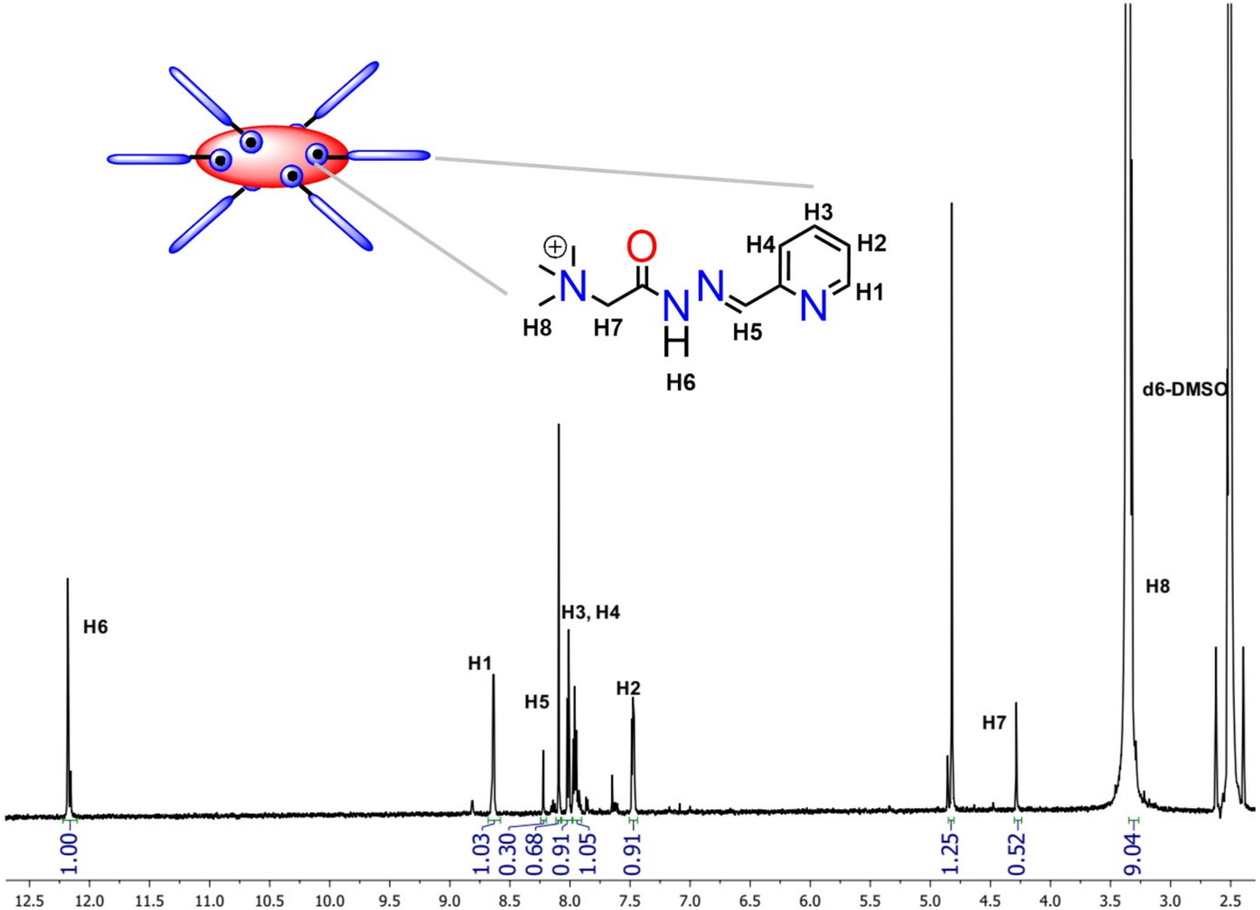


Fig. S24 ^{1}H NMR spectrum (600 MHz, *d6*-DMSO) of **H1**$_{\text{isol}}$

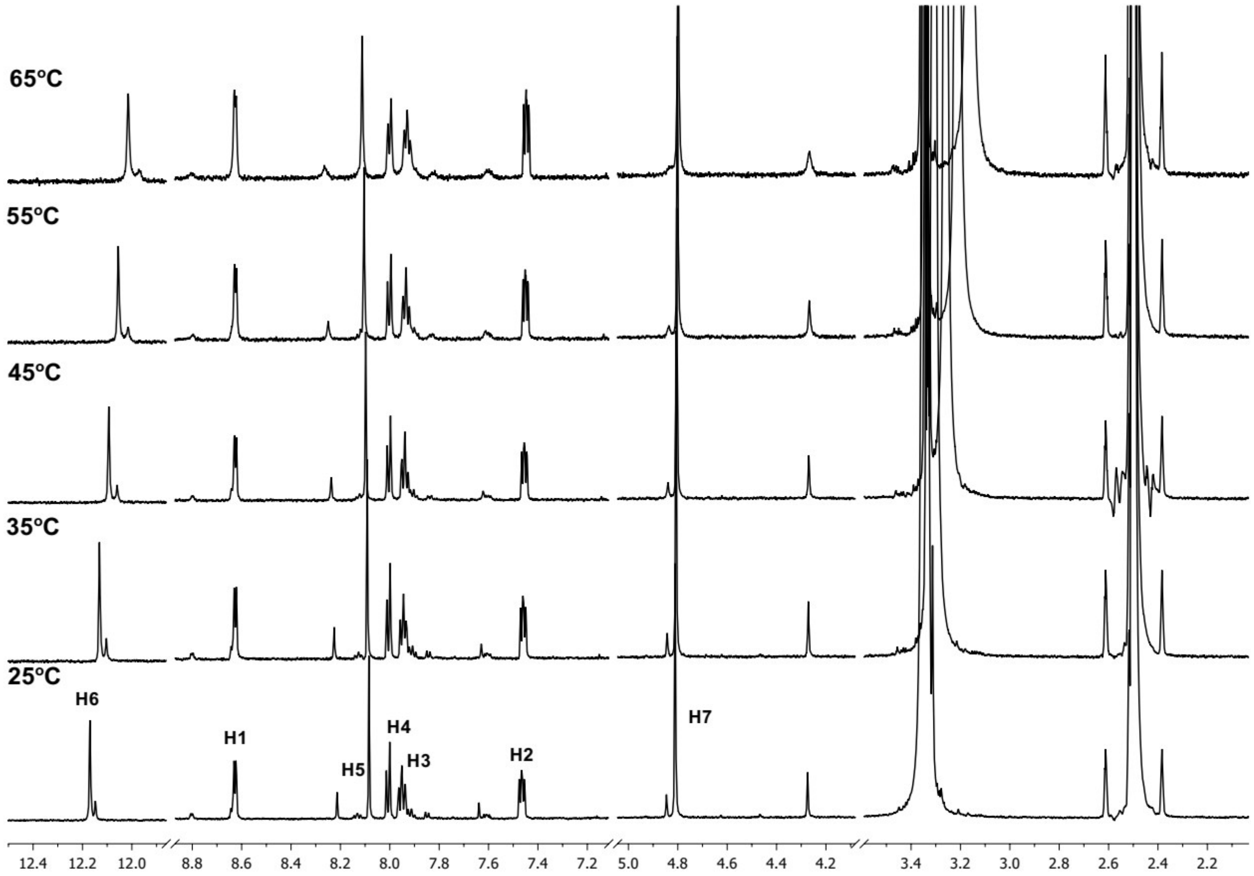


Fig. S25 VT NMR spectrum (600 MHz, *d6*-DMSO) of **H1**$_{\mathbf{isol}}$

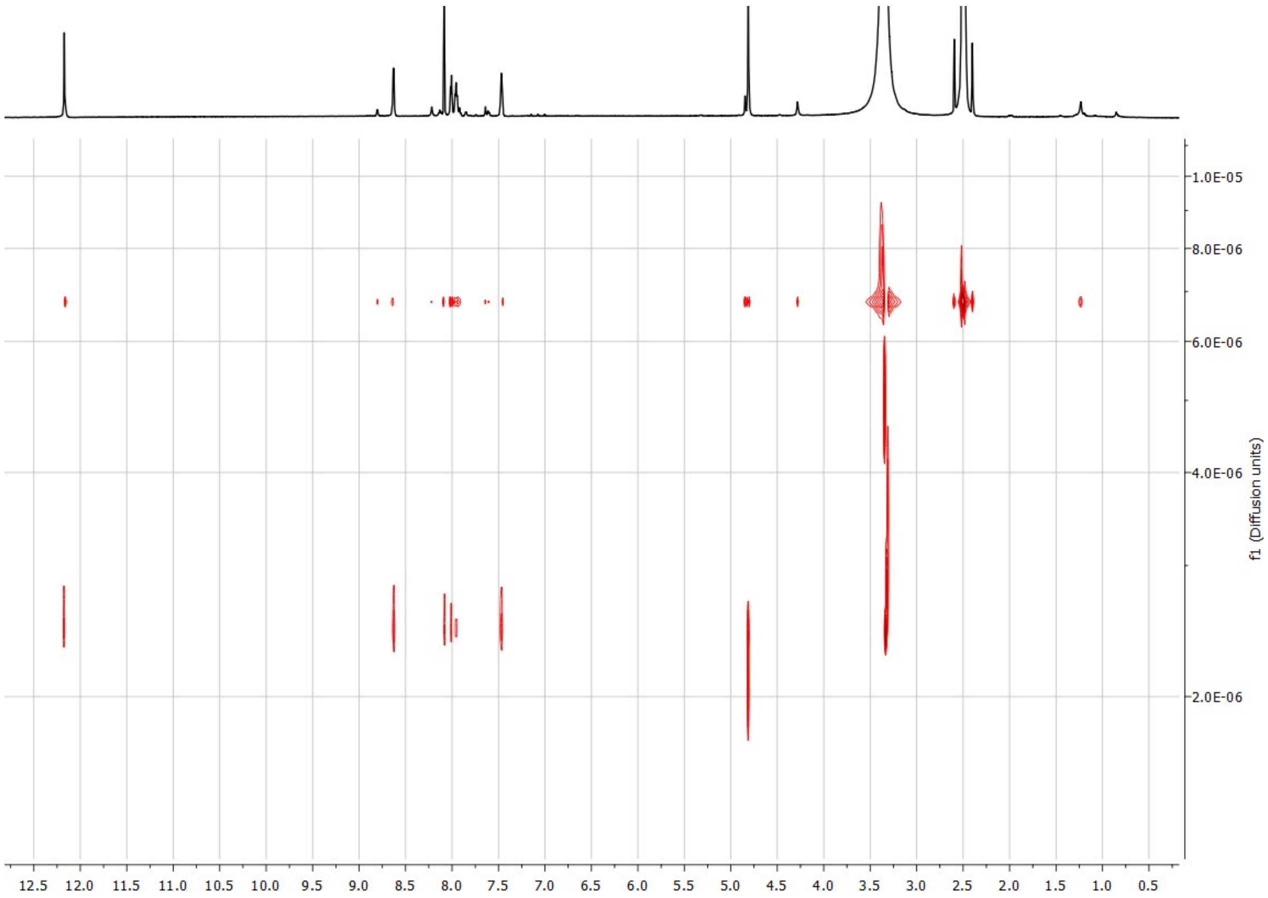


Fig. S26 DOSY NMR spectrum (700 MHz, *d6*-DMSO) of **$H1_{isol}$**

Table S1. Calculated parameters for ligand **L** and **$H1_{isol}$** obtained from DOSY NMR spectroscopy

Entry	Compounds	D [m^2s^{-1}]	r_{sol}[Å]	V_{sph}[$Å^3$]
1	***L***	4.8×10^{-10}	2.29	50.04
2	**H1 [P_2W_{18}-(L)$_6$]**	2.45×10^{-10}	4.48	376.28

S2.3.2. Route A - Synthesis of hybrid $\mathbf{H1_{in\_situ}}$ – SEC – $[P_2W_{18}\text{-}(L)_6]$

Reaction was carried out in NMR tube. To the solution of ligand **L** (0.05 mmol) in 500µl of D_2O appropriate amount of $Na_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ solution were added. After shaking, mixture was subjected to spectroscopic measurements.

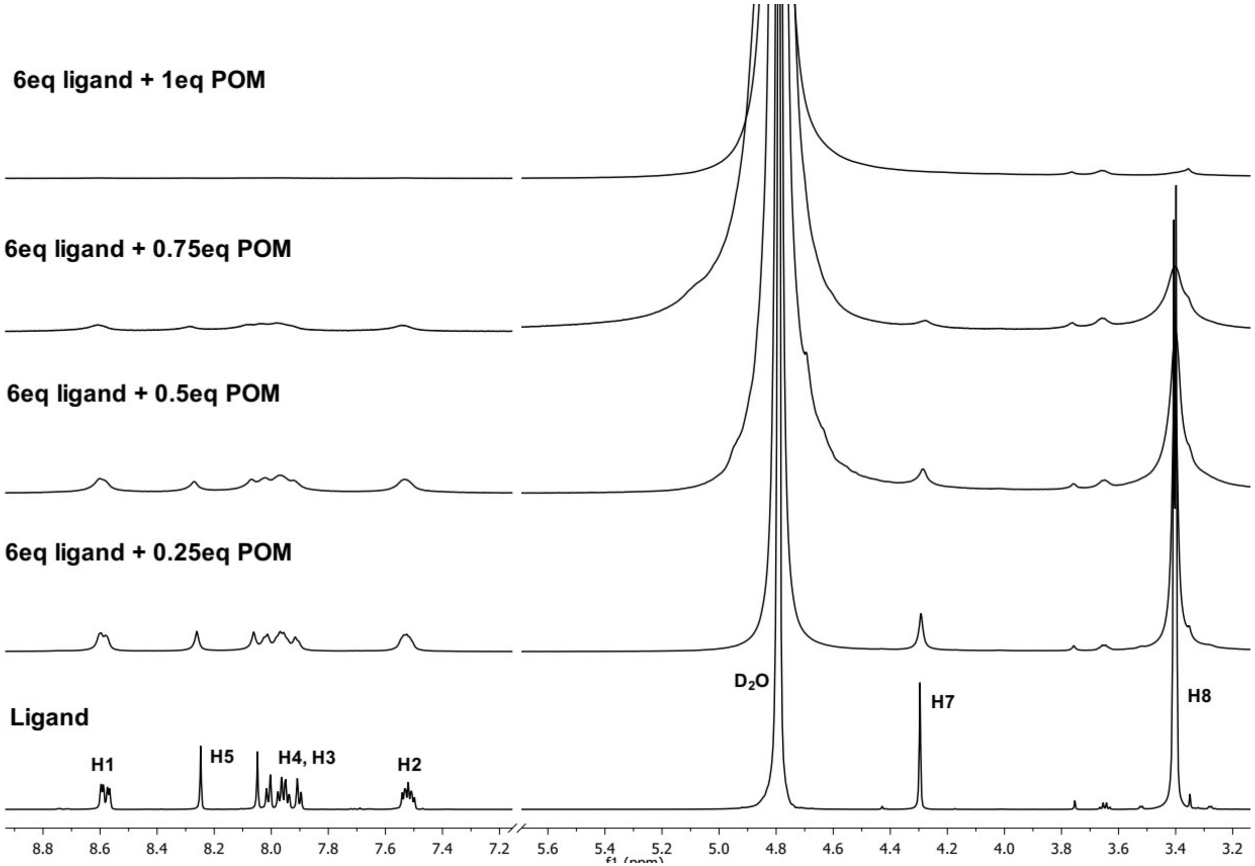


Fig. S27 ^1H NMR spectrum (600 MHz, D_2O) titration of $\mathbf{P_2W_{18}}$ to ligand **L** - formation of $\mathbf{H1_{in\_situ}}$

Upon addition of $Na_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ to the sample containing ligand **L**, a precipitate appeared, suggesting formation of insoluble hybrid **H1**. Addition of 1 eq of $Na_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ resulted in overall formation of H1 assembly, observed as disappearance of signals belonging to free ligand.

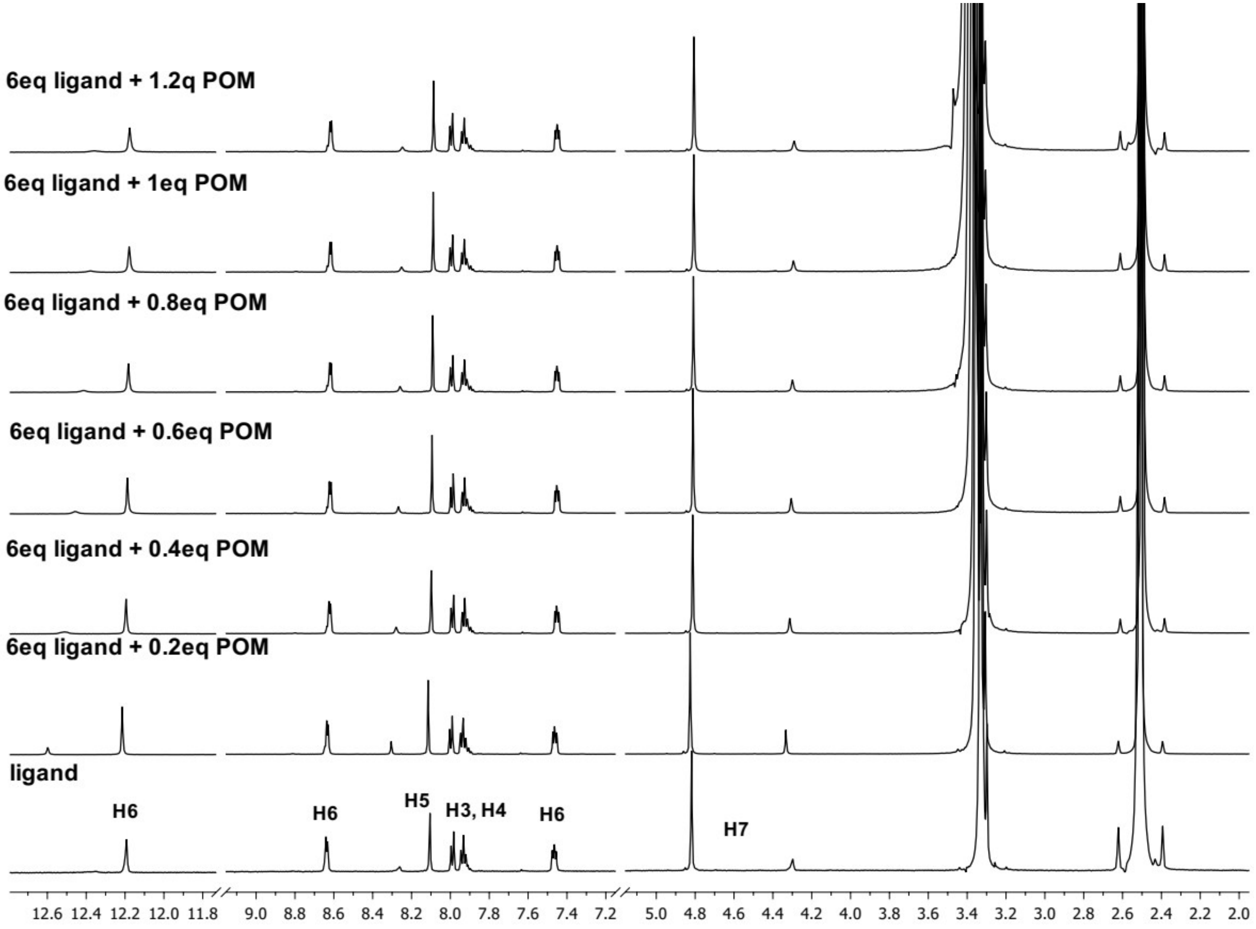


Fig. S28 ^{1}H NMR spectrum (400 MHz, *d6*-DMSO) titration of $\mathbf{P_2W_{18}}$ to ligand **L** - formation of $\mathbf{H1}_{\mathbf{in\_situ}}$

Upon addition of $Na_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ to the sample containing ligand **L**, no visible changes appeared which was confirmed on NMR spectrum presenting lack of changes in chemical shifts and indicate that the assembly H1 did not form in d*6*-DMSO.

S2.3.3. Route B - Synthesis of hybrid $H2_{isol}$ – CD-SEC – $[P_2W_{18}$-$\{L$-$ZnCl_2\}_4]$

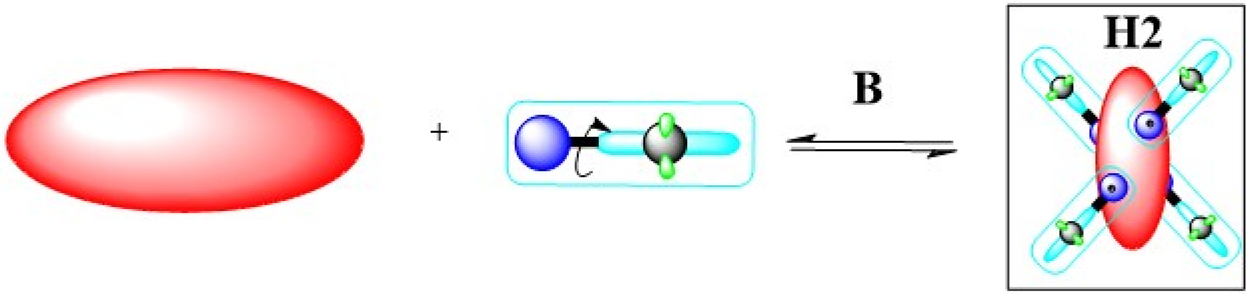


Fig. S29 Schematic representation of route B - synthesis of hybrid **$H2_{isol}$**

$Na_6[\alpha$-$P_2W_{18}O_{62}] \cdot 14H_2O$ (136 mg; 28 μM) was dissolved in 8 ml of mili-Q water what resulted in a clear yellow solution. Next, clear colourless solution of complex ML (60 mg, 168 μM) was prepared in 3 ml of mili-Q water and added to the first one to give not clear, light yellow solution. The mixture was stirred magnetically at room temperature for 48 h to give blue coloured solution and monitored by changes in pH (from 5.79 for POM to 6.02 for hybrid). The final product was centrifuged (3 series of 10 minutes at 4000 rpm), what was followed by washing with water in between the cycles. Obtained product was lyophilized to give blue solid state compound. Yield: 85.34 mg, 54.7% based on ligand **L**. ^{1}H NMR (600 MHz, *d6*-DMSO) δ=8.83-8.80 (m, 1H, **H4**), 8.14-8.12 (t, J^3=7.7, 1H, **H3)** 7.85-7.83 (d, J^2=8.0, 1H, **H1**), 7.63 – 7.60 (m, 2H, **H5+H2**), 4.84 (s, 2H, **H7**), 3.32 (brs, 9H, **H8**)

Elementary analysis

Anal. calc. for $H2_{isol}$: C: 8.55, H: 1.56, N: 3.62%; found: C: 8.48, H: 1.56, N: 3.70%.

Expected formula: $Na_6(C_{11}H_{17}ClN_4OZnCl_2)_4[P_2W_{18}O_{62}] \cdot 14\ H_2O$ = ***$[P_2W_{18}$-$\{L$-$ZnCl_2\}_4]$***

IR

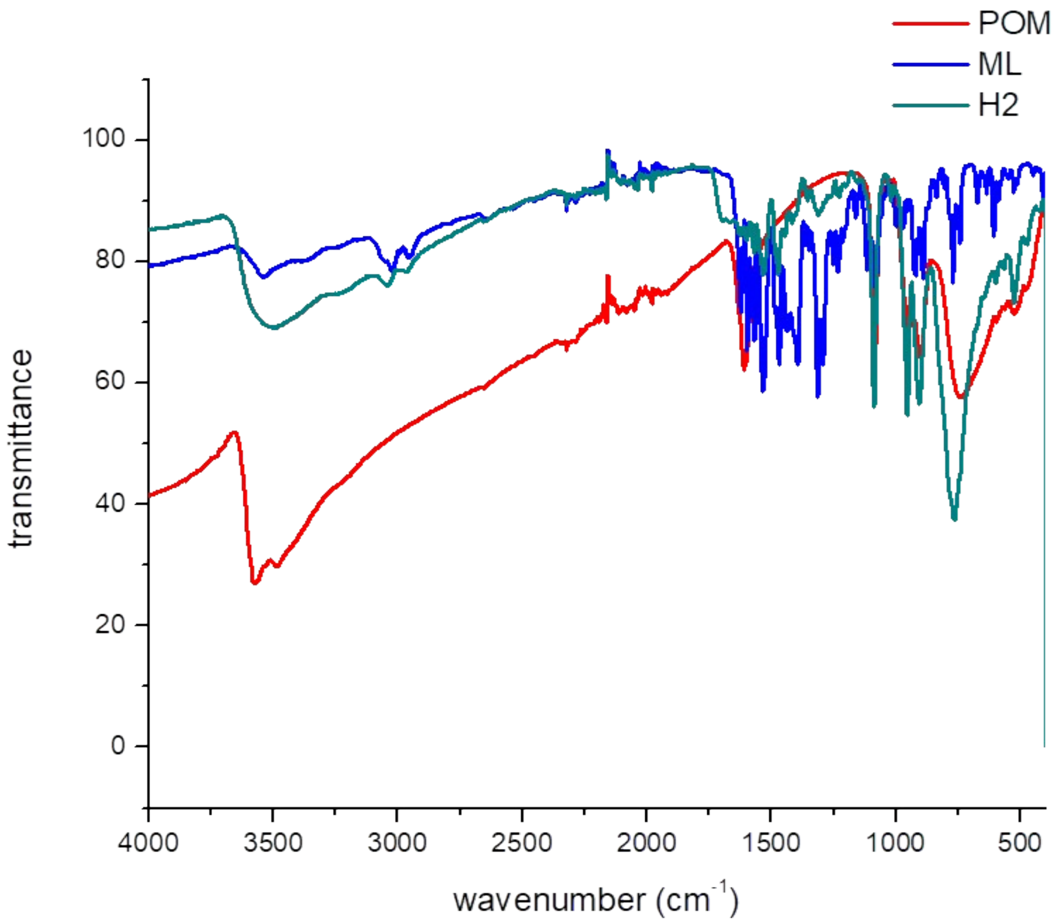


Fig. S30 Superimposed IR spectra of POM, complex [Zn**L**Cl$_2$] and hybrid **H$_2$ [P$_2$W$_{18}$-{L-ZnCl$_2$}$_4$]** in the wavenumber range from 4000 to 500 cm^{-1}

In the IR spectrum one can observe no wavenumbers and peaks N-H from ligand (3453 cm^{-1}) both in complex and in hybrid.

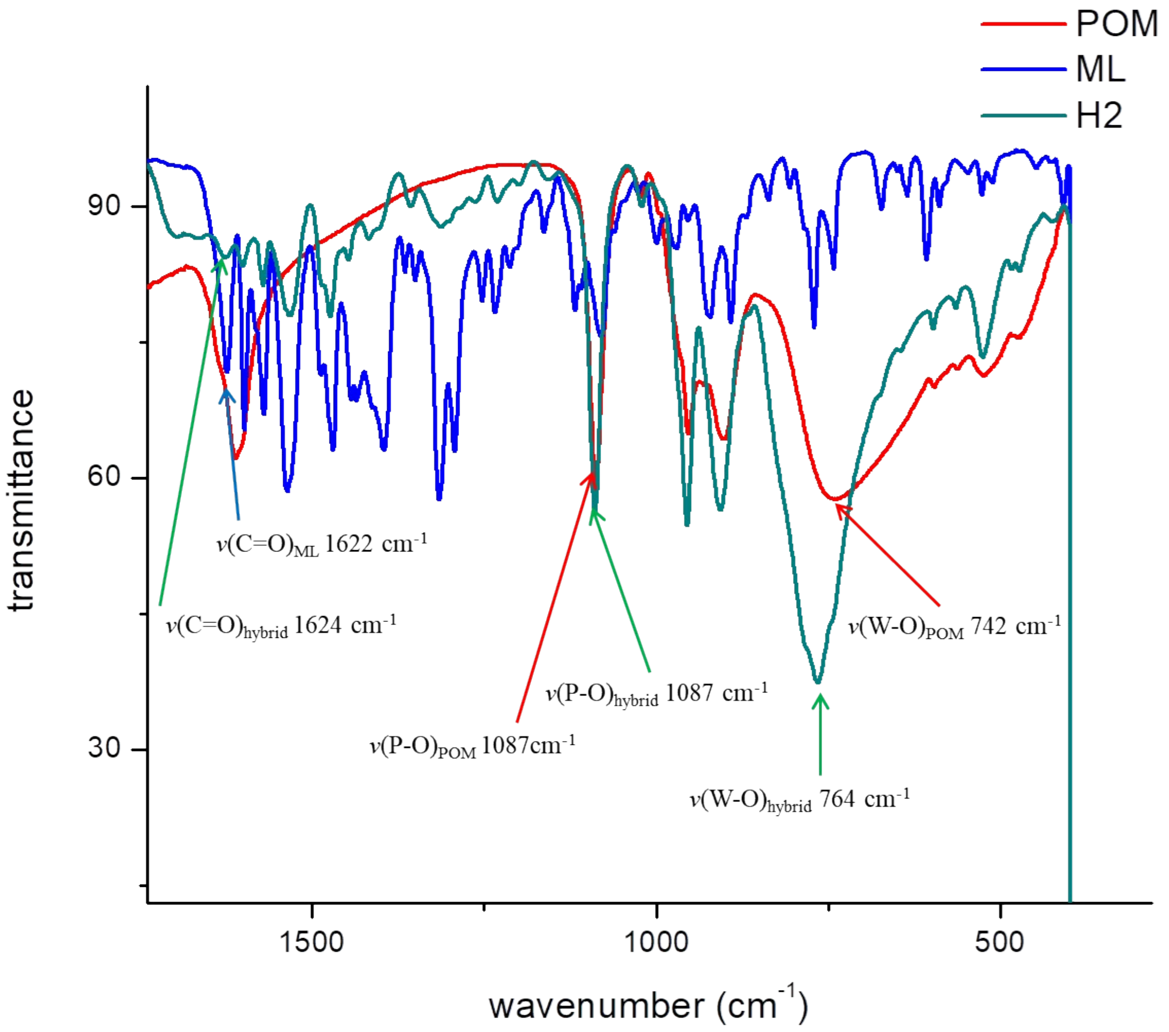


Fig. S31 Superimposed IR spectra of POM, complex [Zn**L**Cl$_2$] and hybrid H$_2$ **[P$_2$W$_{18}$-{L-ZnCl$_2$}$_4$]** in the wavenumber range from 2100 to 300 cm^{-1}

In the IR spectrum one can observe wavenumbers and peaks from C=O in 1622 cm^{-1} for complex and 1624 cm^{-1} for hybrid, P-O are in range of 1087 cm^{-1} for POM and hybrid what determined stability of POM. Peak from W-O in POM is in 742 cm^{-1} and in 764 cm^{-1} from hybrid, what is a confirmation of creation of hybrid.

TGA (thermogravimetric analysis)

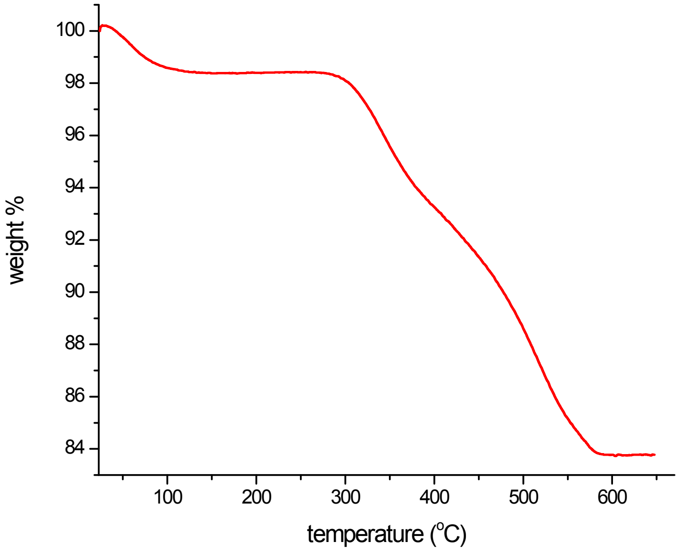


Fig. S32 TGA diagrams of **H2 [P_2W_{18}-{L-$ZnCl_2$}$_4$]**

In TGA analysis we observed that weight% is lower around 100°C because of water disappeared, the next decreasing value is about organic compound decomposition (complexes). Difference between starting and ending value is around 16% what has an explanation in that: mass of hybrid is around 6275.86, mass of four complexes 1426.24 so this 16% is almost equal to mass of complexes.

Dynamic Light Scattering (DLS)

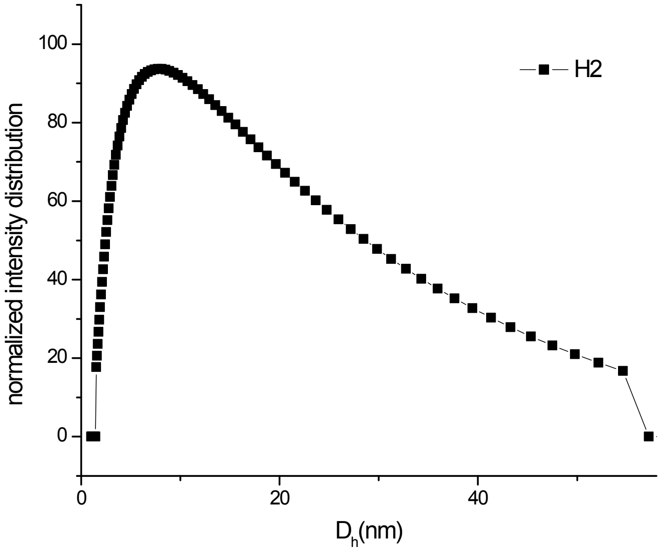


Fig. S33 Dynamic light scattering (DLS) diagram of **H2 $[P_2W_{18}$-{L-$ZnCl_2\}_4]$**

Dynamic light scattering (DLS) measurement shows that **$[P_2W_{18}$-{L-$ZnCl_2\}_4]$** appear as individual molecules with a maximum hydrodynamic distribution (D_h) concentrated around 10 nm. The distribution of measurements is up to the value around 60 nm. Moreover, stable **$[P_2W_{18}$-{L-$ZnCl_{2\}4}]$** assemblies with spherical shapes are obtained by dropping the solution of assemblies on silicon surface (Fig. S35).

Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS)

1. Solid

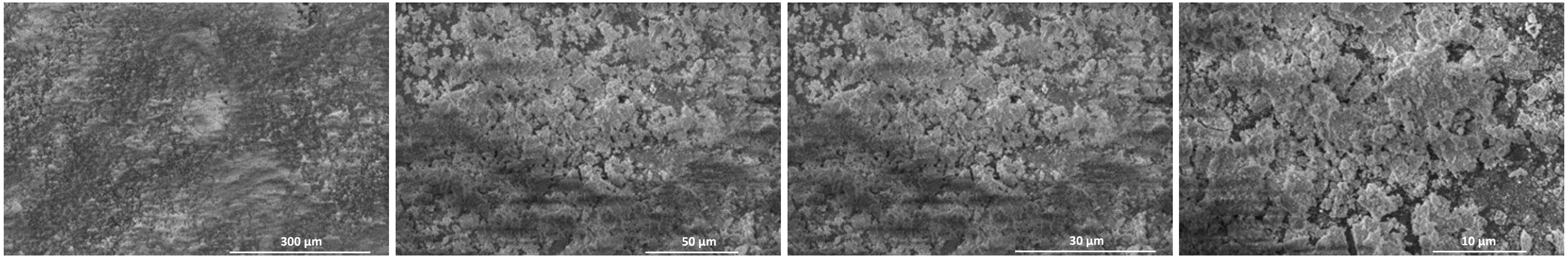


Fig. S34 Scanning electron microscopy (SEM) images of solid **[P_2W_{18}-{L-$ZnCl_2$}$_4$]** assemblies.

2. Drop-casting:

a) dissolved in DMSO and evaporated

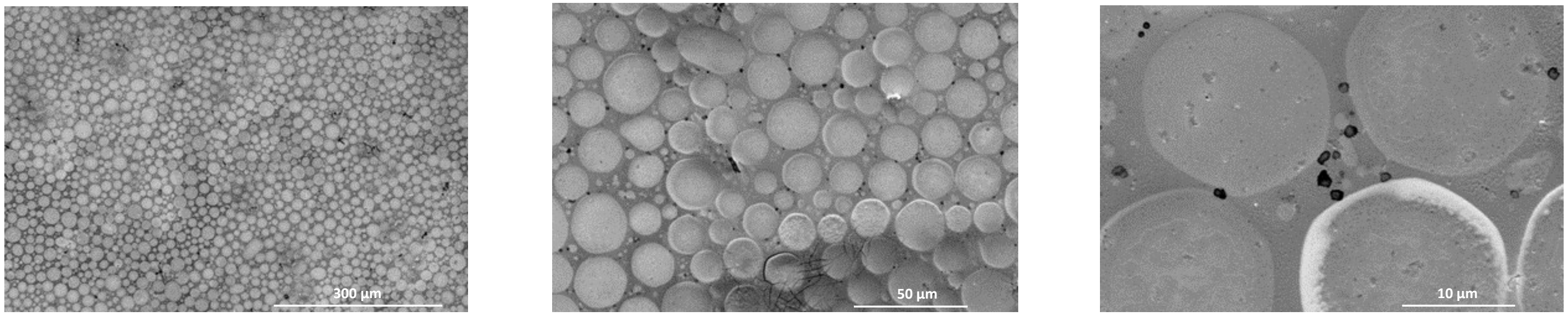


Fig. S35 Scanning electron microscopy (SEM) images of evaporated **[P_2W_{18}-{L-$ZnCl_2$}$_4$]** assemblies.

b) dissolved in DMSO and heated

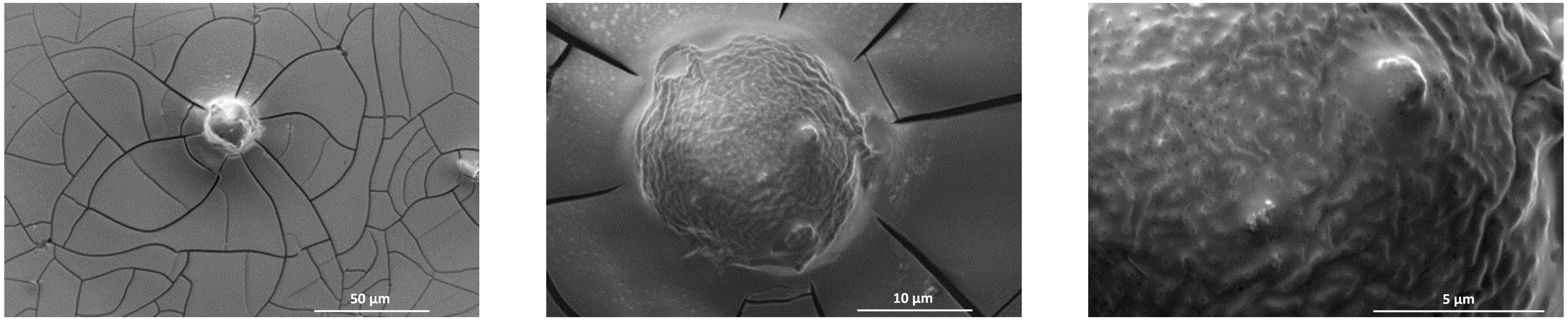
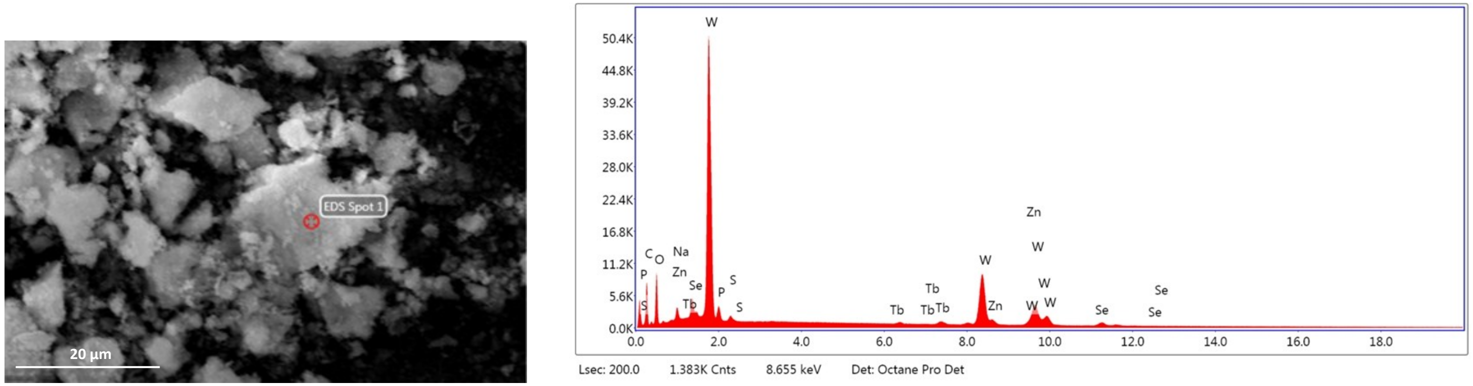
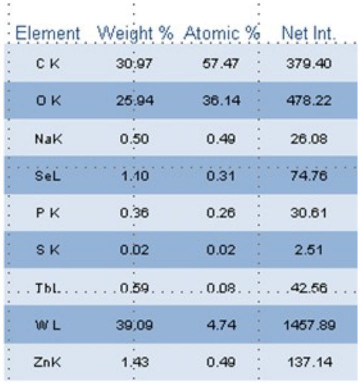


Fig. S36 Scanning electron microscopy (SEM) images of heated **[P_2W_{18}-{L-$ZnCl_2$}$_4$]** assemblies.

3. EDS





Element	Weight %	Atomic %	Net Int.
C K	30.97	57.47	379.40
O K	25.94	36.14	478.22
NaK	0.50	0.49	26.08
SeL	1.10	0.31	74.76
P K	0.36	0.26	30.61
S K	0.02	0.02	2.51
TbL	0.59	0.08	42.56
W L	39.09	4.74	1457.89
ZnK	1.43	0.49	137.14

Fig. S37 Scanning electron microscopy (SEM) image of **[P_2W_{18}-{L-$ZnCl_2$}$_4$]** POM and its X-ray energy dispersion spectrum.

4. EDAX

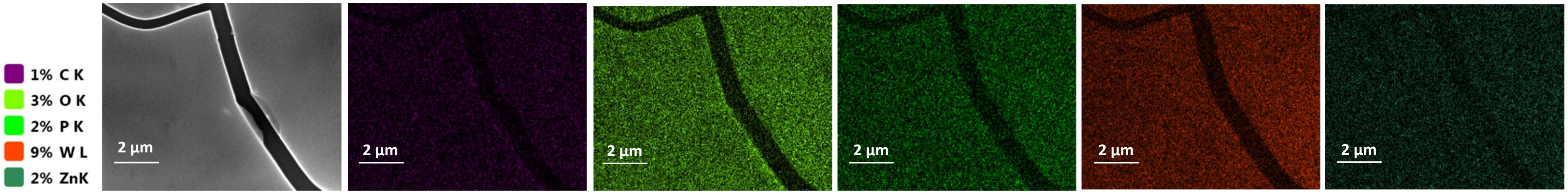


Fig. S38 EDAX analysis of **H2** in DMSO.

At SEM image one can observe layered surface of hybrid **$[P_2W_{18}\text{--}\{\text{L-ZnCl}_2\}_4]$** with aggregation in solid state. In turn, when sample was dissolved in DMSO and evaporated one can note another type of morphology – samples are orientated in a kind of spherical assemblies. In case of heated samples of POM there are cavities in whole surface. Energy Dispersive Spectroscopy (EDS) shows that anticipated elements like tungsten, phosphorus, oxygen, carbon and zinc are present in the studied sample.

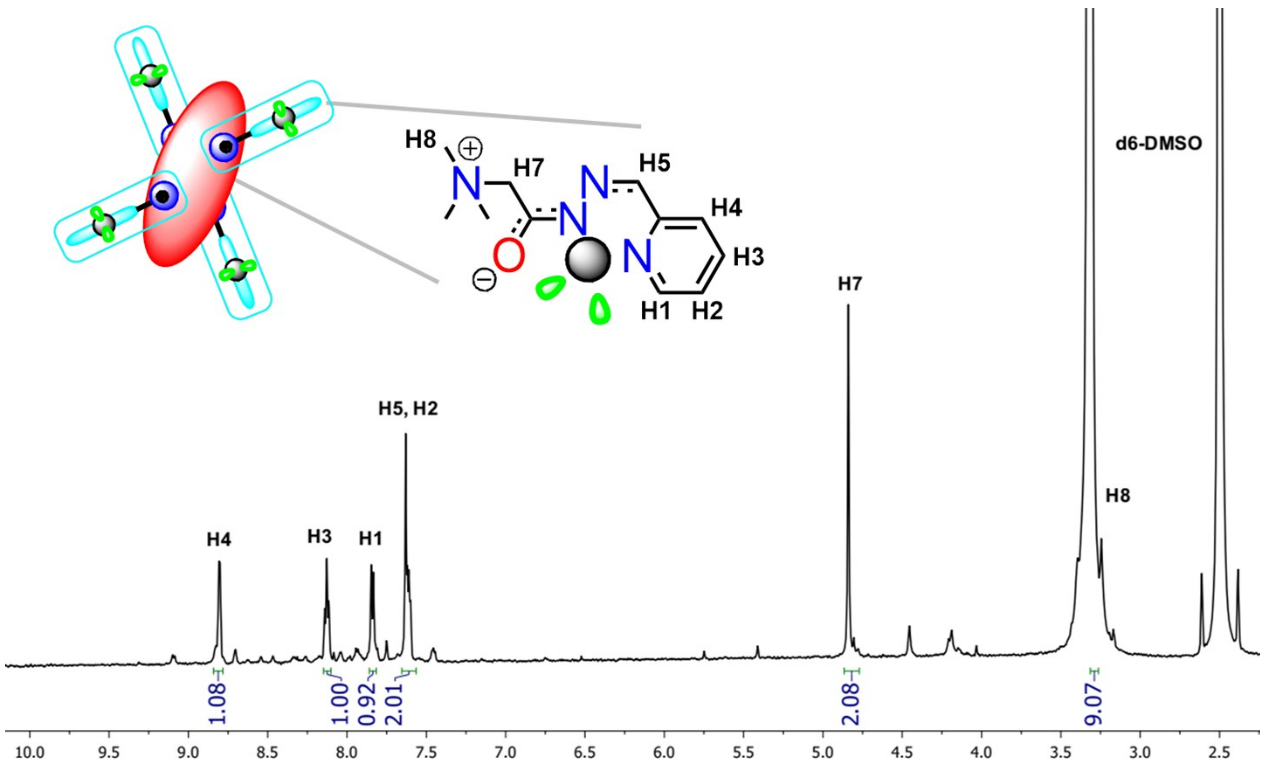


Fig. S39 ^{1}H NMR spectrum (600 MHz, *d6*-DMSO) of **H2$_{isol}$**

S2.3.4. Route B - Synthesis of hybrid $H2_{in\_situ}$ – CD-SEC – $[P_2W_{18}\text{-}\{L\text{-}ZnCl_2\}_4]$

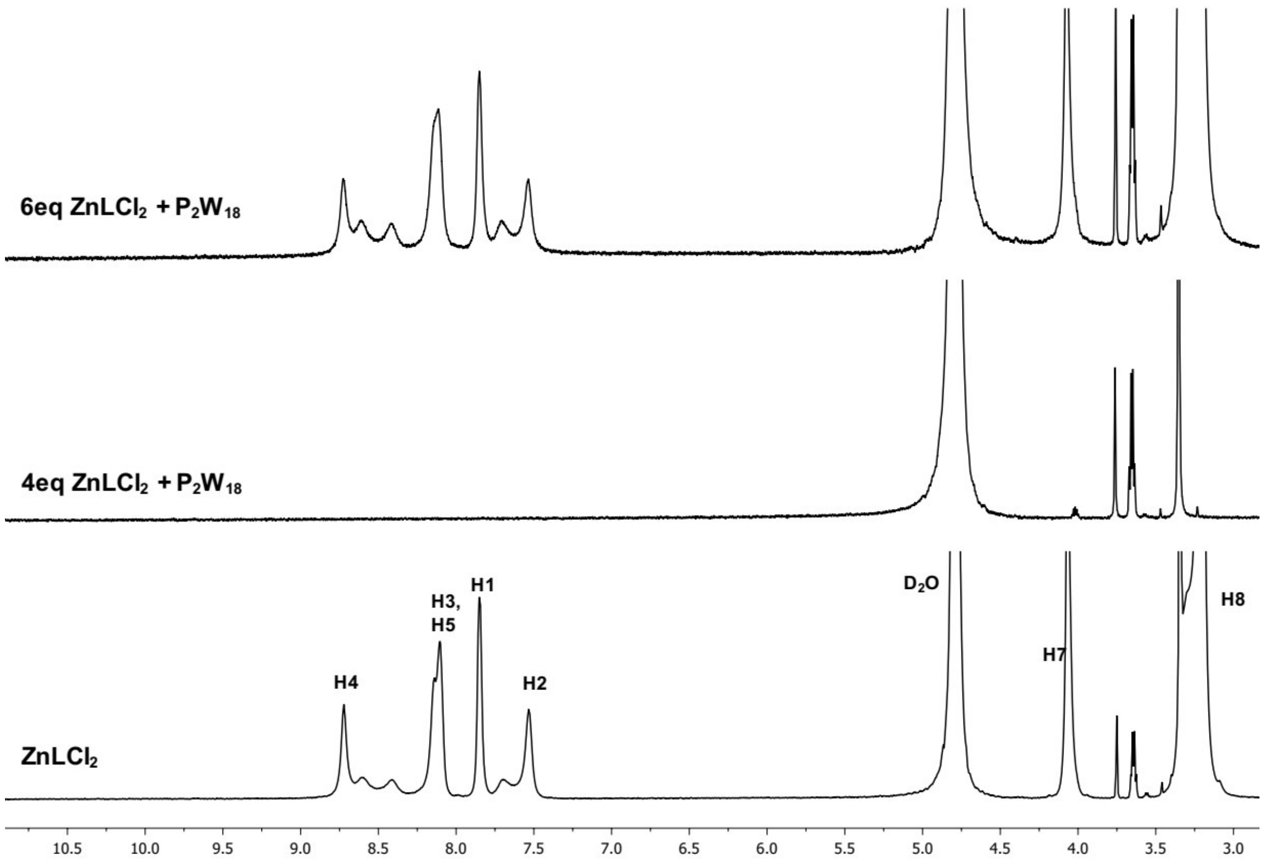


Fig. S40 ^{1}H NMR spectrum (600 MHz, D_2O) titration of $\mathbf{P_2W_{18}}$ to solution of complex $[Zn\mathbf{L}Cl_2]$ - formation of $\mathbf{H2_{in\_situ}}$

S2.3.5. Route C - Synthesis of hybrid $H3_{isol}$ – CD-SEC – $[P_2W_{18}\text{-}(L)_6\text{-}\{Zn(ClO_4)_2\}_3]$

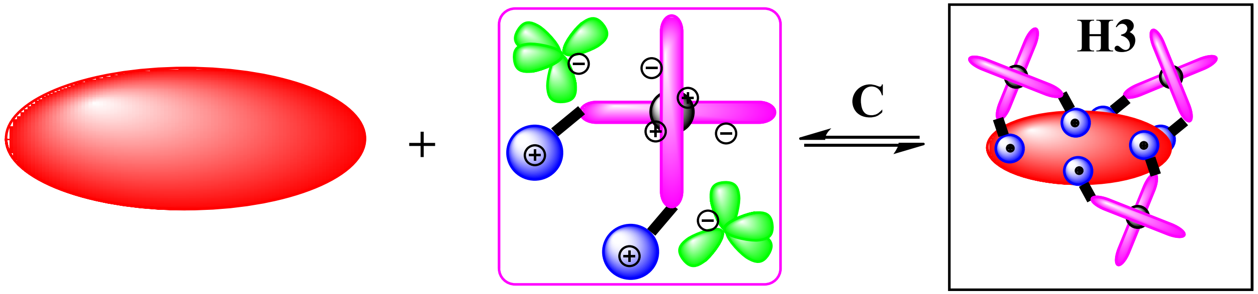


Fig. S41 Schematic representation of route C - synthesis of hybrid $\mathbf{H3_{isol}}$

$Na_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ (230.41 mg; 47.5 μM) was dissolved in 20 ml of mili-Q water what resulted in a clear yellow solution (pH 5.92). Next, clear colourless solution of complex M**L**$_2$ (99.7 mg, 142.5 μM) was prepared in 12.5 ml of mili-Q water and added to the first one to give light yellow, cloudy solution. The mixture was stirred magnetically at room temperature for 48 h to give blue coloured solution (pH 6.11). The final product was centrifuged (3 series of 10 minutes at 4000 rpm), what was followed by washing with water in between the cycles. Obtained product was lyophilized to give blue solid state compound. Yield: 133.7 mg, 47.7% based on ligand **L.** ^{1}H NMR (600 MHz, *d6*-DMSO) δ=8.78 (s, 1H, **H5**), 8.13-8.10 (t, J^3=7.26, 1H, **H3)** 8.04-8.03 (d, J^2=4.25, 1H, **H4**), 7.91 – 7.90 (d,J=7.39 1H, **H1**), 7.54-7.52 (m, 1H, **H2**), 4.20-5.15 (m, 2H, **H7**), 3.22 (m, 9H, **H8**)

Elementary analysis

Anal. calc. for $H3_{isol}$: C: 11.19, H: 1.85, N: 4.74%; found: C: 11.15, H: 1.78, N: 4.68%.

Expected formula: $Na_6(C_{11}H_{17}ClN_4O)_6(ZnCl_2O_8)_3[P_2W_{18}O_{62}] \cdot 14\ H_2O$ = $\mathbf{[P_2W_{18}\text{-}(L)_6\text{-}(Zn(ClO_4)_2)_3]}$

IR

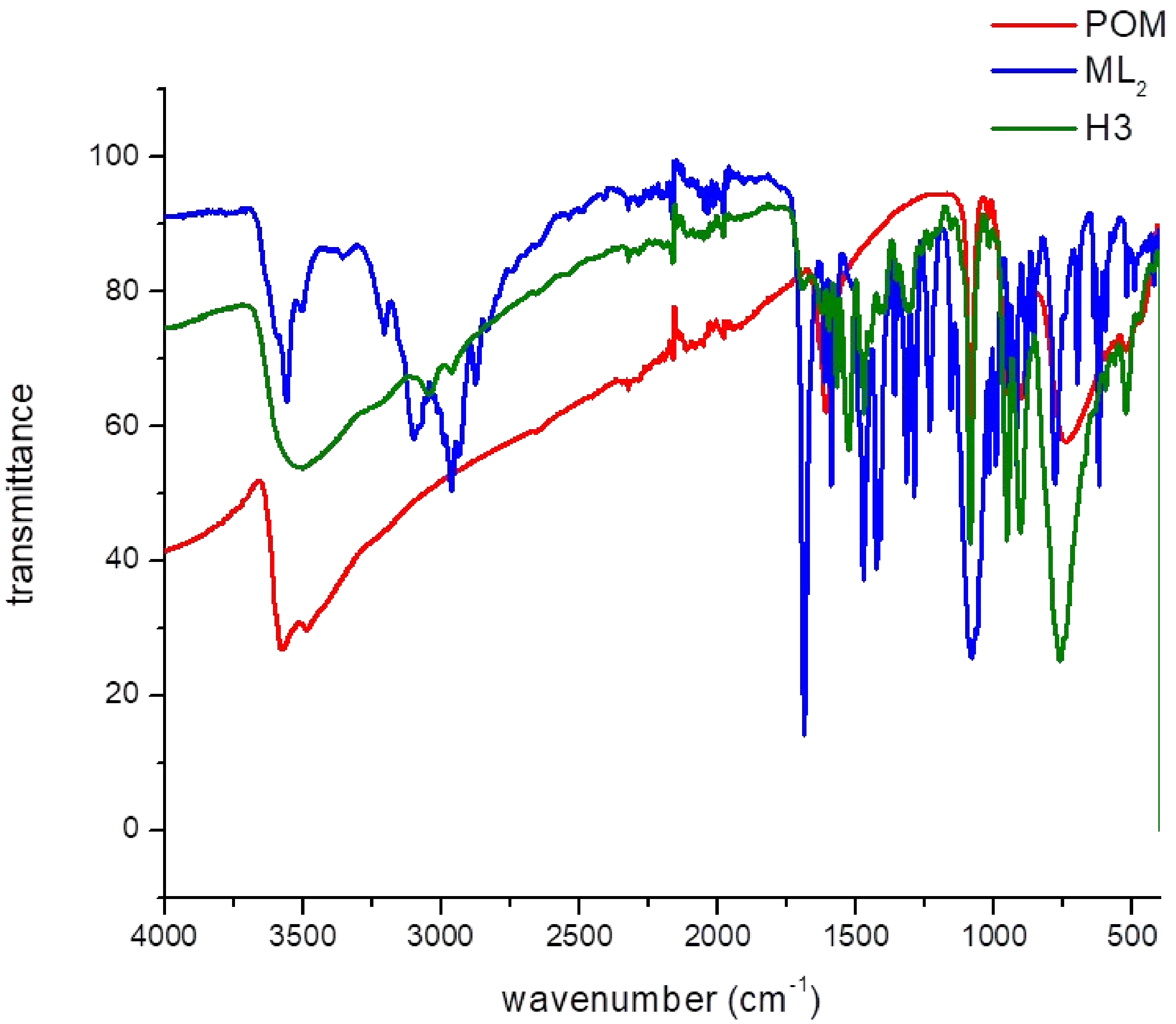


Fig. S42 Superimposed IR spectra of POM, complex [Zn**L**$_2$(ClO$_4$)$_2$] and hybrid **H3 [P$_2$W$_{18}$-(L)$_6$-(Zn(ClO$_4$)$_2$)$_3$]** in the wavenumber range from 4000 to 400 cm^{-1}

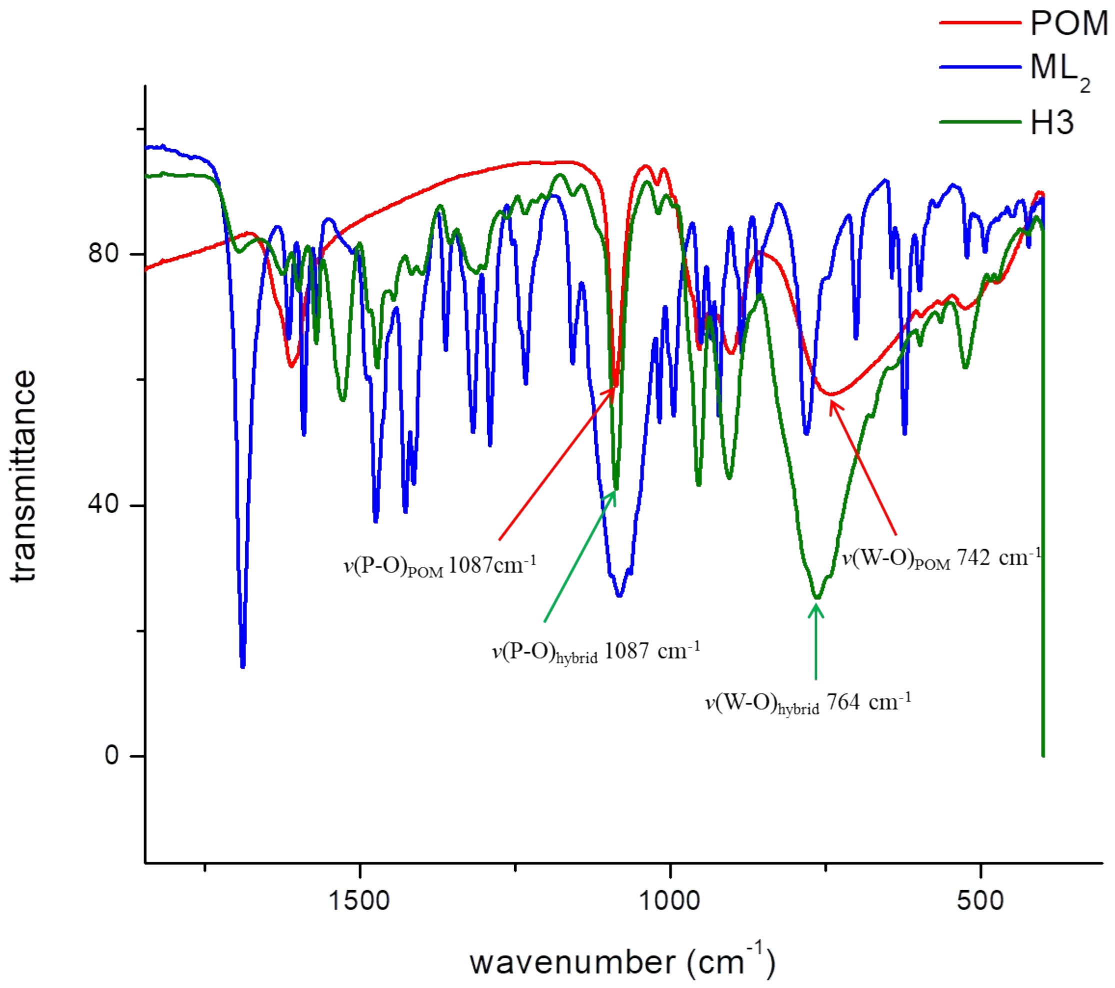


Fig. S43 Superimposed IR spectra of POM, complex [Zn**L**$_2$(ClO$_4$)$_2$] and hybrid **H3** **$[P_2W_{18}\text{-}(L)_6\text{-}(Zn(ClO_4)_2)_3]$** in the wavenumber range from 2100 to 300 cm^{-1}

In the IR spectrum one can observe wavenumbers and peaks form P-O are in of 1087 cm^{-1} for POM and hybrid. Peak form W-O in POM is in 742 cm^{-1} and in 764 cm^{-1} from hybrid, what is a confirmation of creation of hybrid.

TGA (thermogravimetric analysis)

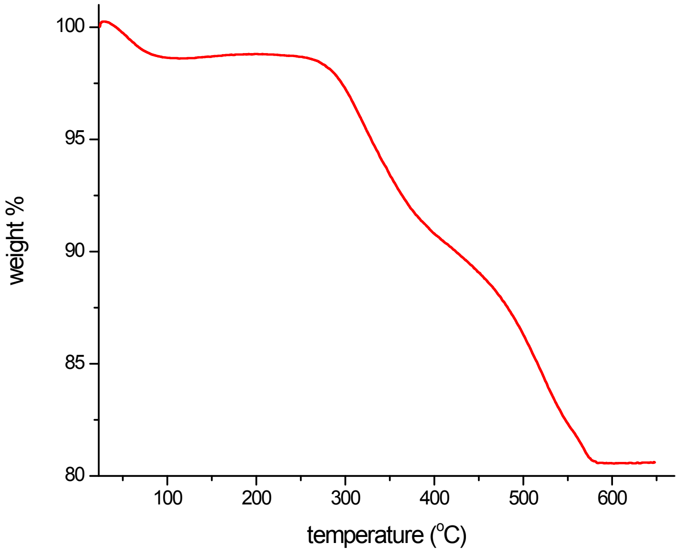


Fig. S44 TGA diagrams of hybrid **H3** **[P_2W_{18}-(L)$_6$-(Zn(ClO_4)$_2$)$_3$]**

In TGA analysis we observed that weight% is lower around 100°C because of water disappeared, the next decreasing value is about organic compound decomposition (complexes). Difference between starting and ending value is around 20% what has an explanation in that: mass of hybrid is around 7000, mass of six ligands is around 1500 so this 20% is almost equal to mass of ligands.

Dynamic Light Scattering (DLS)

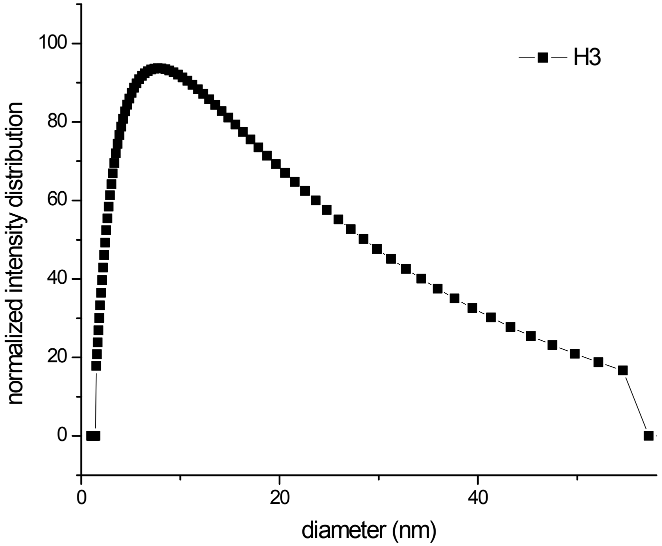


Fig. S45 Dynamic light scattering (DLS) diagram of **H3 [P_2W_{18}-(L)$_6$-(Zn(ClO_4)$_2$)$_3$]**.

Dynamic light scattering (DLS) measurement shows that **[P_2W_{18}-(L)$_6$-(Zn(ClO_4)$_2$)$_3$]** appear as individual molecules with a maximum hydrodynamic distribution (D_h) concentrated around 10 nm. The distribution of measurements is up to the value around 60 nm. Moreover, stable **[P_2W_{18}-(L)$_6$-(Zn(ClO_4)$_2$)$_3$]** assemblies with spherical shapes are obtained by dropping the solution of assemblies on silicon surface (Fig. S47). However, upon closer inspection their character seems to be dissipated and more prone for merging and aggregation into higher order assemblies.

Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) and EDAX

1. Solid

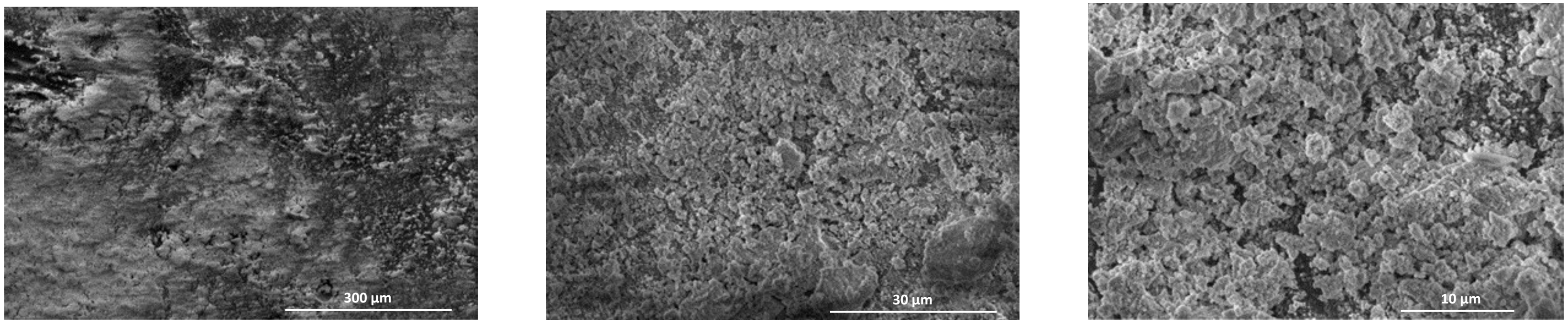


Fig. S46 Scanning electron microscopy (SEM) images of solid **H3 $[P_2W_{18}\text{-}(L)_6\text{-}(Zn(ClO_4)_2)_3]$** assemblies.

2. Drop-casting:

a) dissolved in DMSO and evaporated

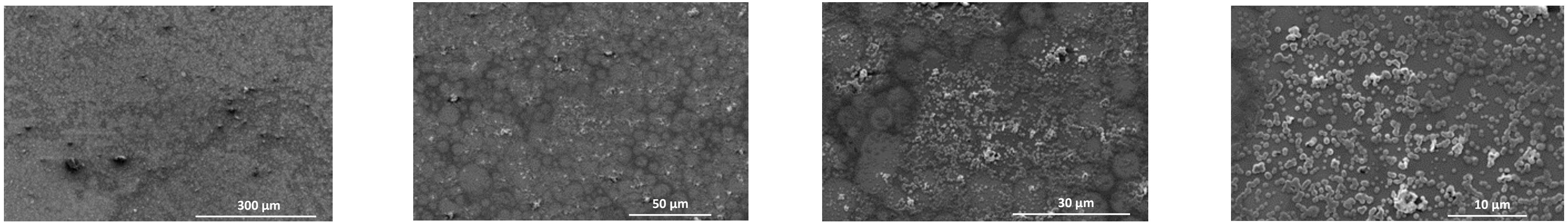


Fig. S47 Scanning electron microscopy (SEM) images of evaporated **H3 $[P_2W_{18}\text{-}(L)_6\text{-}(Zn(ClO_4)_2)_3]$** assemblies.

b) dissolved in DMSO and heated

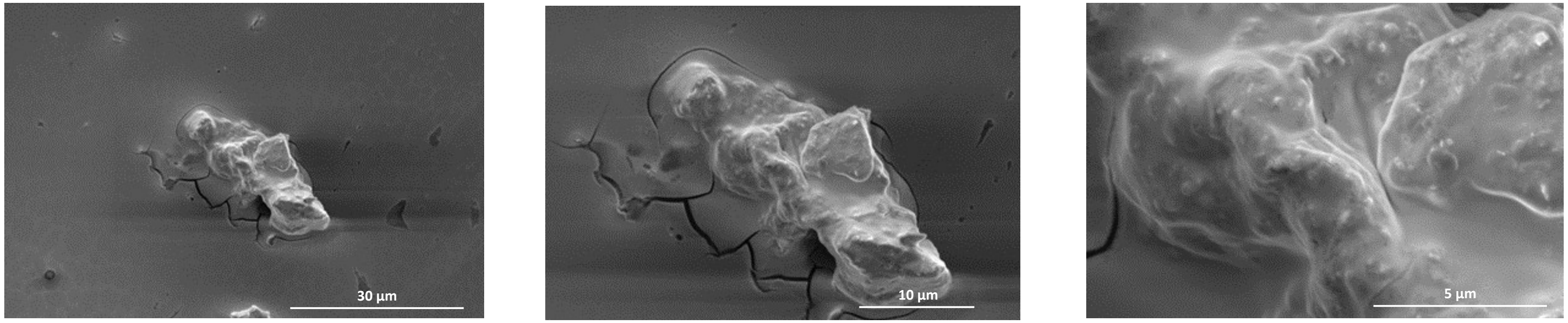
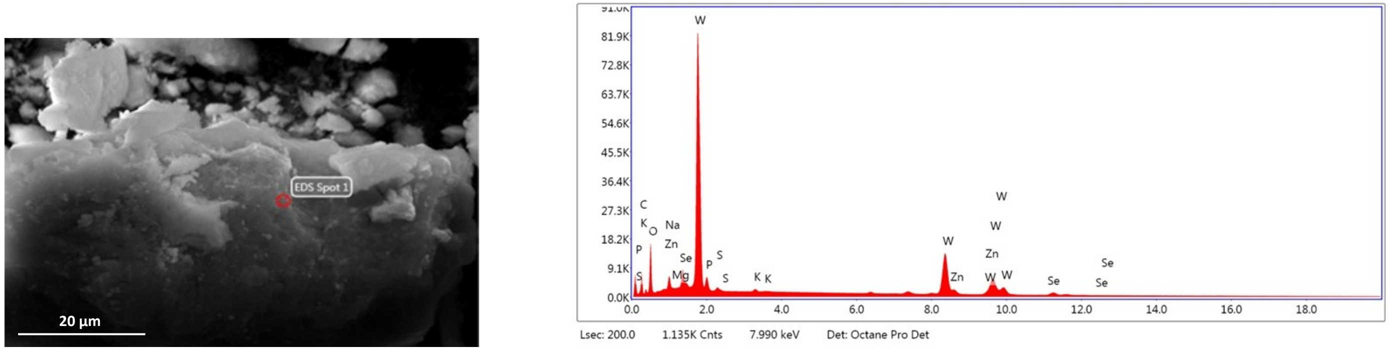
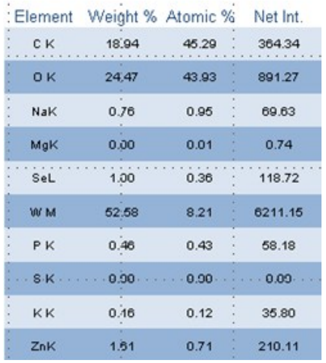


Fig. S48 Scanning electron microscopy (SEM) images of heated **H3 $[P_2W_{18}\text{-}(L)_6\text{-}(Zn(ClO_4)_2)_3]$** assemblies.

3. EDS





Element	Weight %	Atomic %	Net Int.
C K	18.94	45.29	364.34
O K	24.47	43.93	891.27
NaK	0.76	0.95	69.63
MgK	0.00	0.01	0.74
SeL	1.00	0.36	118.72
W M	52.58	8.21	6211.15
P K	0.46	0.43	58.18
S K	0.00	0.00	0.00
K K	0.16	0.12	35.80
ZnK	1.61	0.71	210.11

Fig. S49 Scanning electron microscopy (SEM) image of **H3 $[P_2W_{18}\text{-}(L)_6\text{-}(Zn(ClO_4)_2)_3]$** hybrid and its X-ray energy dispersion spectrum.

4. EDAX

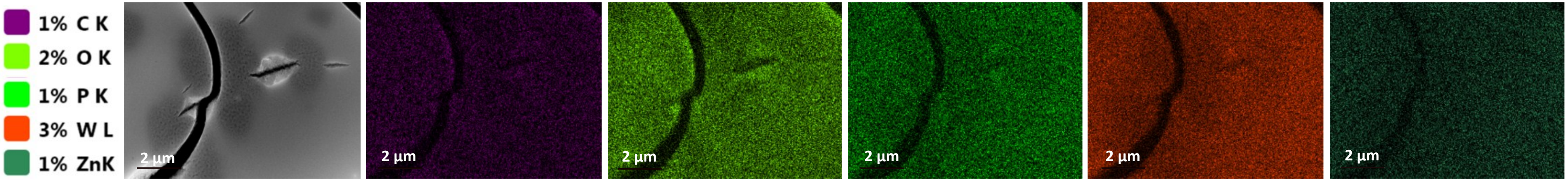


Fig. S50 EDAX analysis of **H3** in DMSO.

At SEM image one can observe layered surface of hybrid **$[P_2W_{18}-(L)_6-(Zn(ClO_4)_2)_3]$** with aggregation in solid state. In turn, when sample was dissolved in DMSO and evaporated one can note another type of morphology – sample are orientated in spherical rings. In case of heated samples of POM there is more homogenic surface. Energy Dispersive Spectroscopy (EDS) shows that anticipated elements like tungsten, phosphorus, oxygen, carbon and zinc are present in the studied sample.

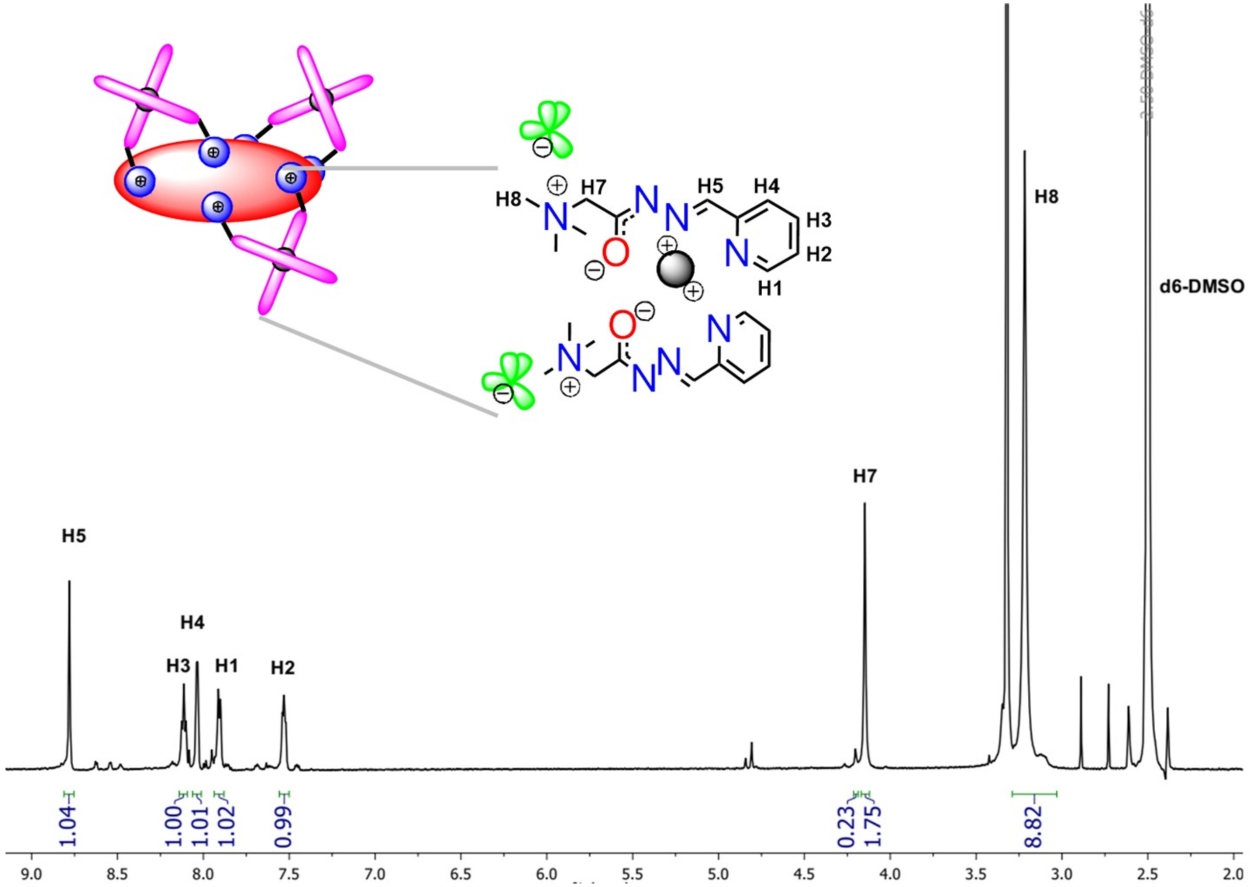


Fig. S51 ^{1}H NMR spectrum (600 MHz, *d6*-DMSO) of **H3**$_{\text{isol}}$

S2.3.6. Route C - Synthesis of hybrid $H3_{in\_situ}$ – CD-SEC –$[P_2W_{18}$-$(L)_6$-$(Zn(ClO_4)_2)_3]$

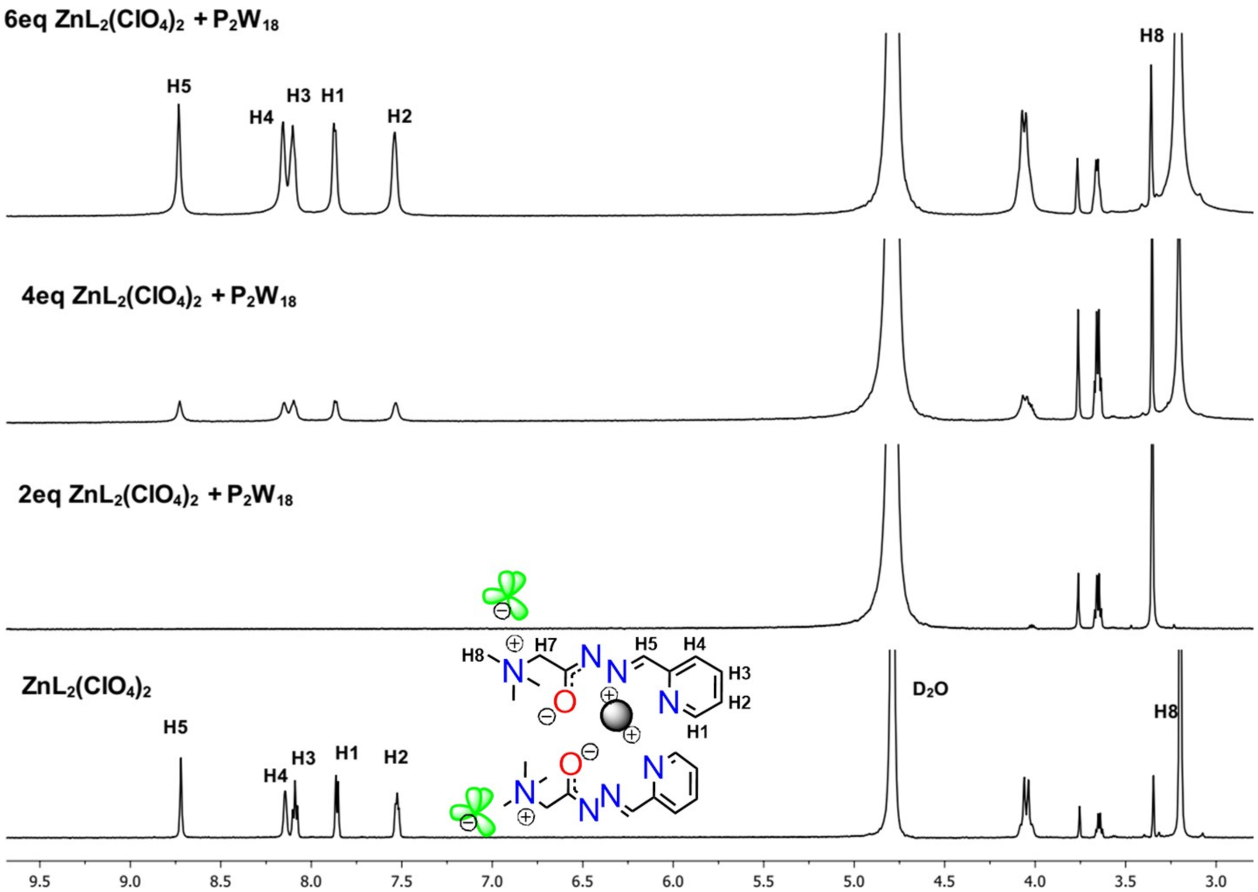


Fig. S52 ^{1}H NMR spectrum (600 MHz, D_2O) titration of $\mathbf{P_2W_{18}}$ to solution of complex $[Zn\mathbf{L_2}(ClO_4)_2]$ - formation of $\mathbf{H3_{in\_situ}}$

S2.3.7. Route D - Synthesis of hybrid – H2$_{isol/D}$

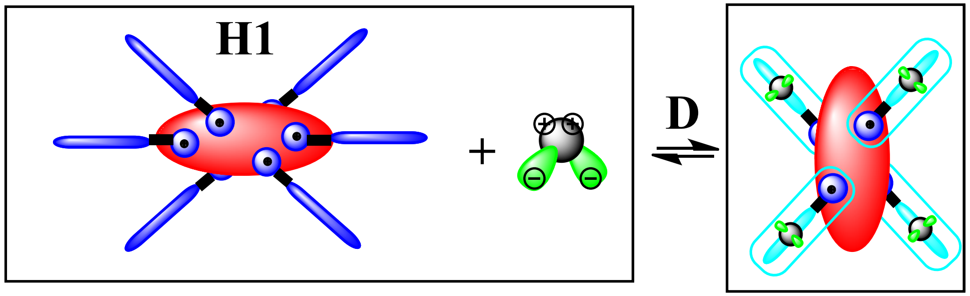


Fig. S53 Schematic representation of route D - synthesis of hybrid **H2$_{isol/D}$**

Hybrid **H1** (15 mg; 2.45 μM) was dissolved in 5 ml of mili-Q water what resulted in a cloudy blue solution. Next, triethylamine (1.3 μl; 9.38 μM) was added (pH 8.11) and the last step was addition of zinc chloride (1.24 mg, 9.09 μM). The mixture was stirred magnetically at room temperature for 48 h to give blue coloured solution with precipitation. The final product was centrifuged (3 series of 10 minutes at 4000 rpm), what was followed by washing with water in between the cycles. Obtained product was lyophilized to give blue solid state compound. Yield: 9.30 mg, 57.70% based on hybrid **H1**.

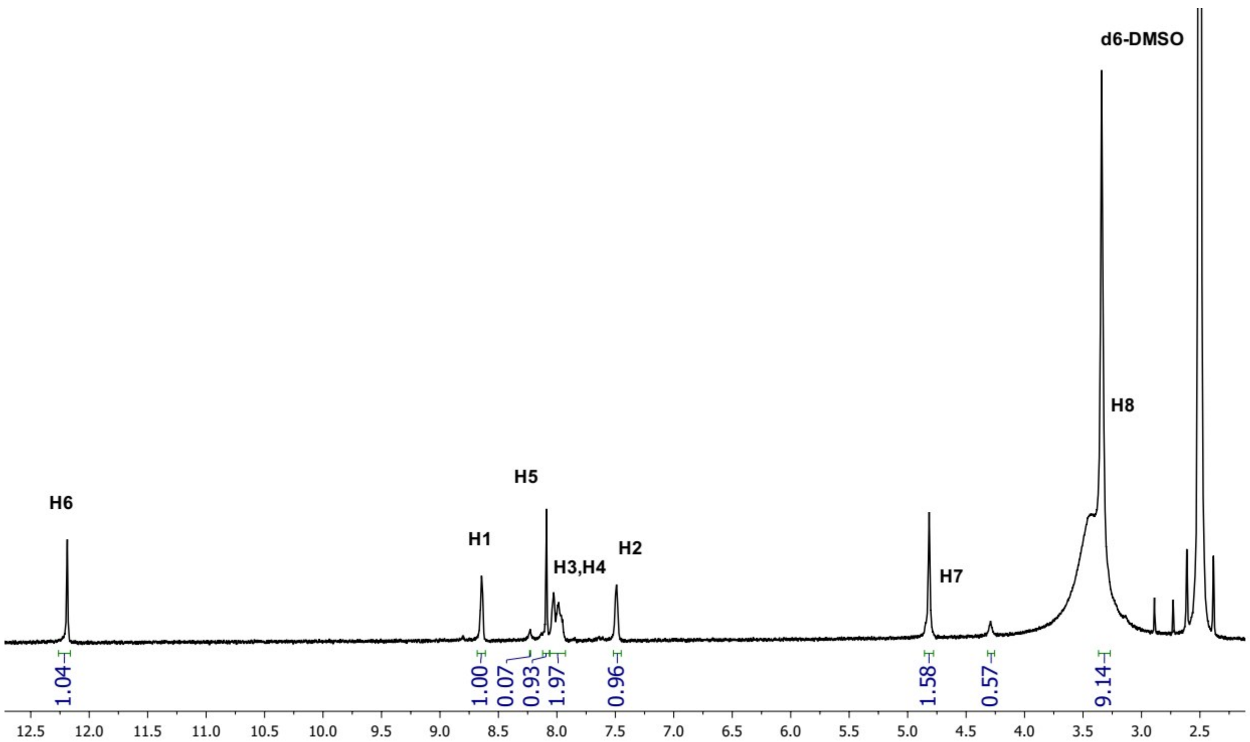


Fig. S54 ^{1}H NMR spectrum (600 MHz, *d6*-DMSO) of **H2**$_{\mathbf{isol/D}}$

Chemical shift the same as for **H1** – product **H2**$_{\mathbf{isol/D}}$ did not form

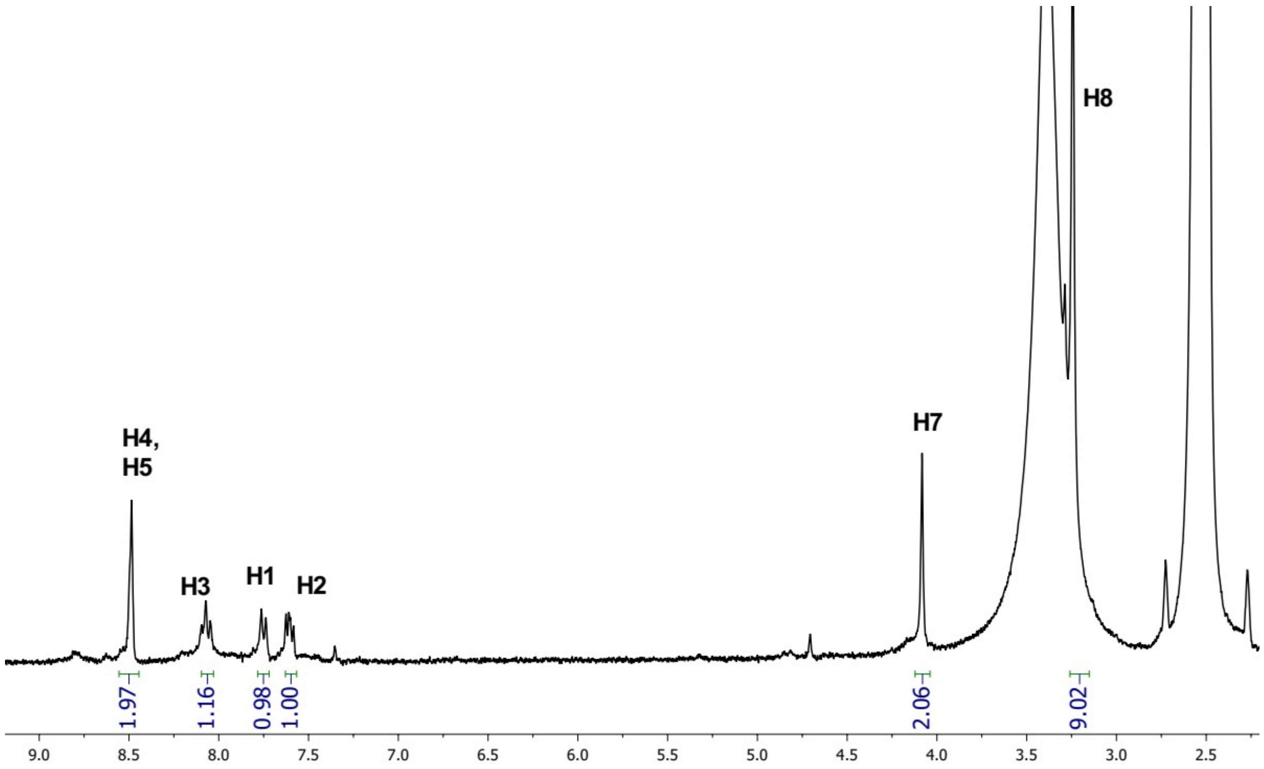


Fig. S55 ^{1}H NMR spectrum (600 MHz, *d6*-DMSO) of **H2**$_{\mathbf{in\_situ/D}}$

H2$_{\mathbf{in\_situ}}$ in *d6*-DMSO – chemical shifts correspond to complex [Zn**L**Cl$_2$], hybrid **H2** did not formed

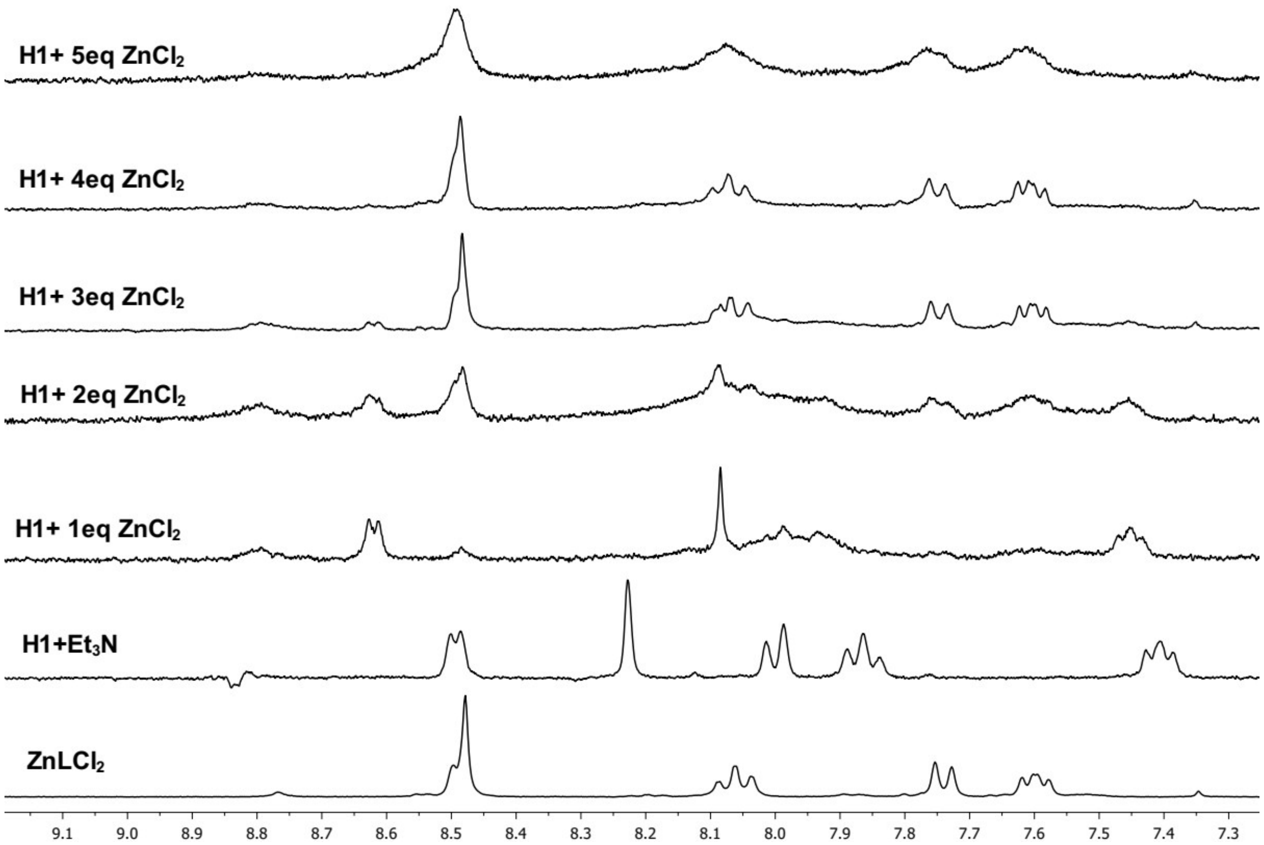


Fig. S56 ^1H NMR spectrum (600 MHz, *d6*-DMSO) titration of complex [Zn**L**Cl_2] to solution of $\mathbf{H1}_{\mathbf{isol}}$ - formation of $\mathbf{H2}_{\mathbf{in\_situ/D}}$

$\mathbf{H2}_{\mathbf{in\_situ}}$ in *d6*-DMSO titration – chemical shifts correspond to complex [Zn**L**Cl_2], hybrid **H2** did not form.

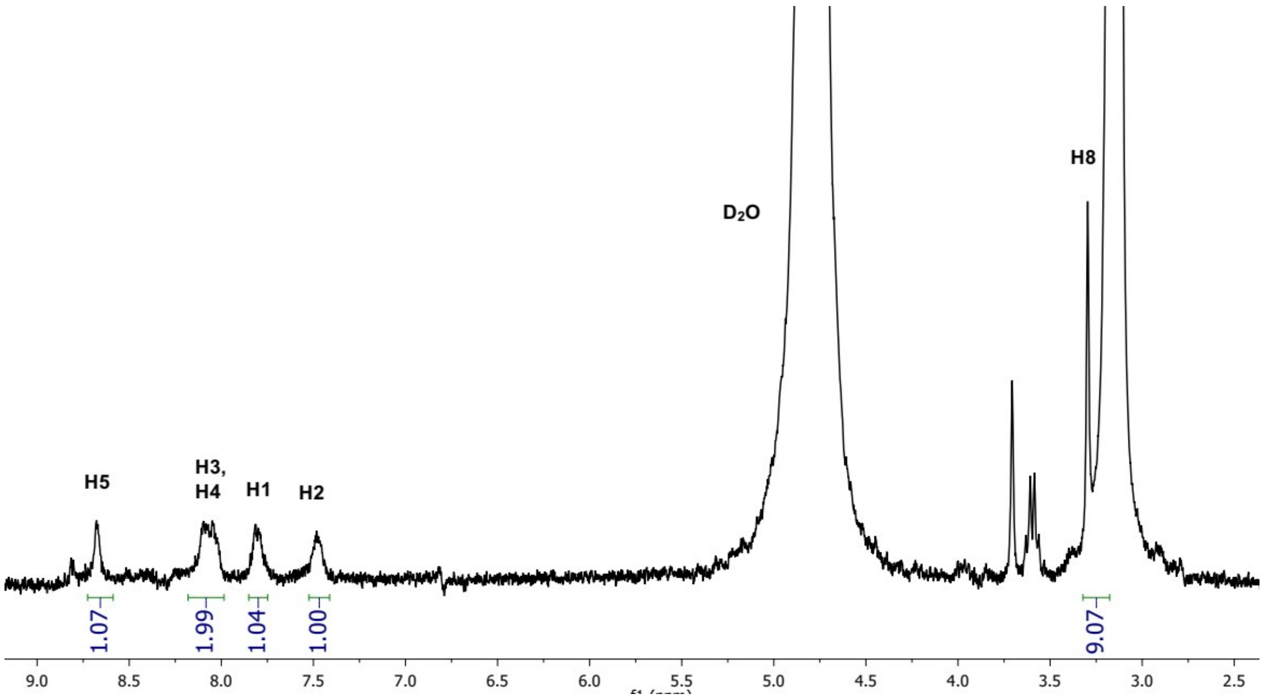


Fig. S57 ^{1}H NMR spectrum (600 MHz, D_2O) formation of **H2**$_{in\_situ/D}$

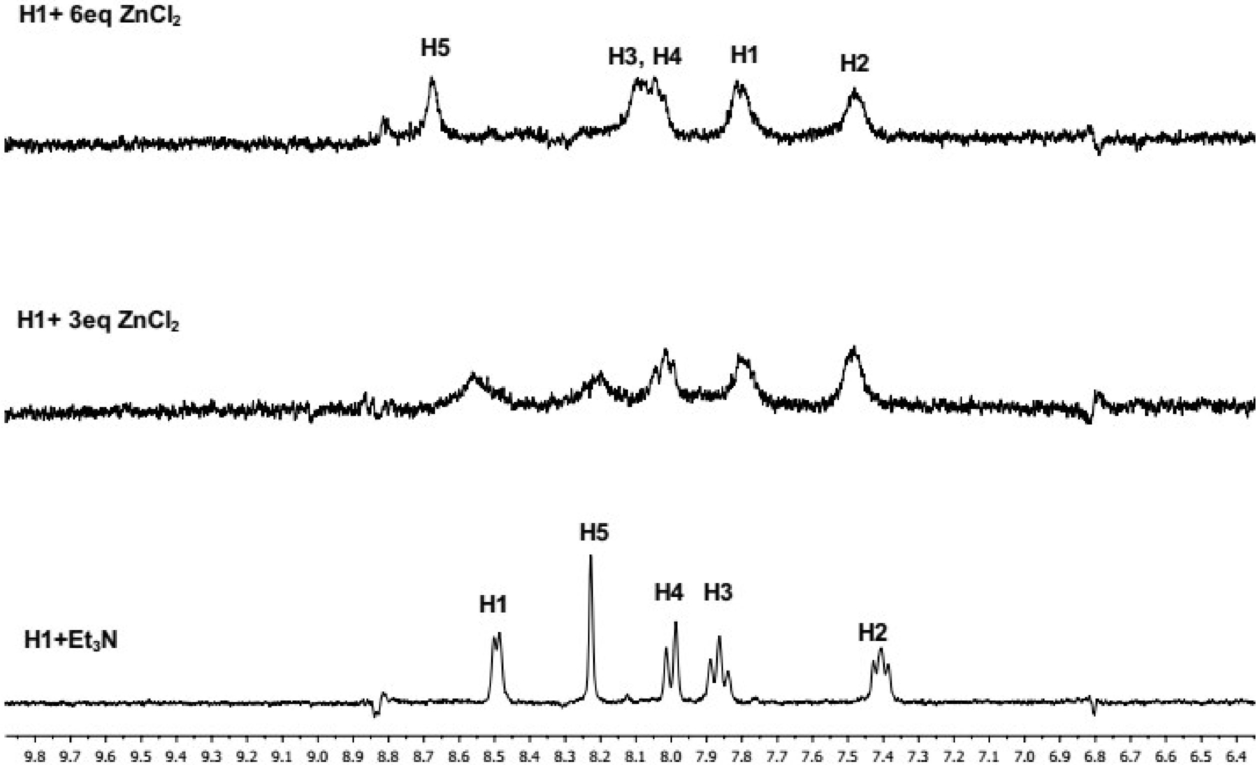


Fig. S58 ^{1}H NMR spectrum (600 MHz, D_2O) titration of solution of **H1$_{isol}$** with $ZnCl_2$ - formation of **H2$_{in\_situ/D}$** (aromatic region)

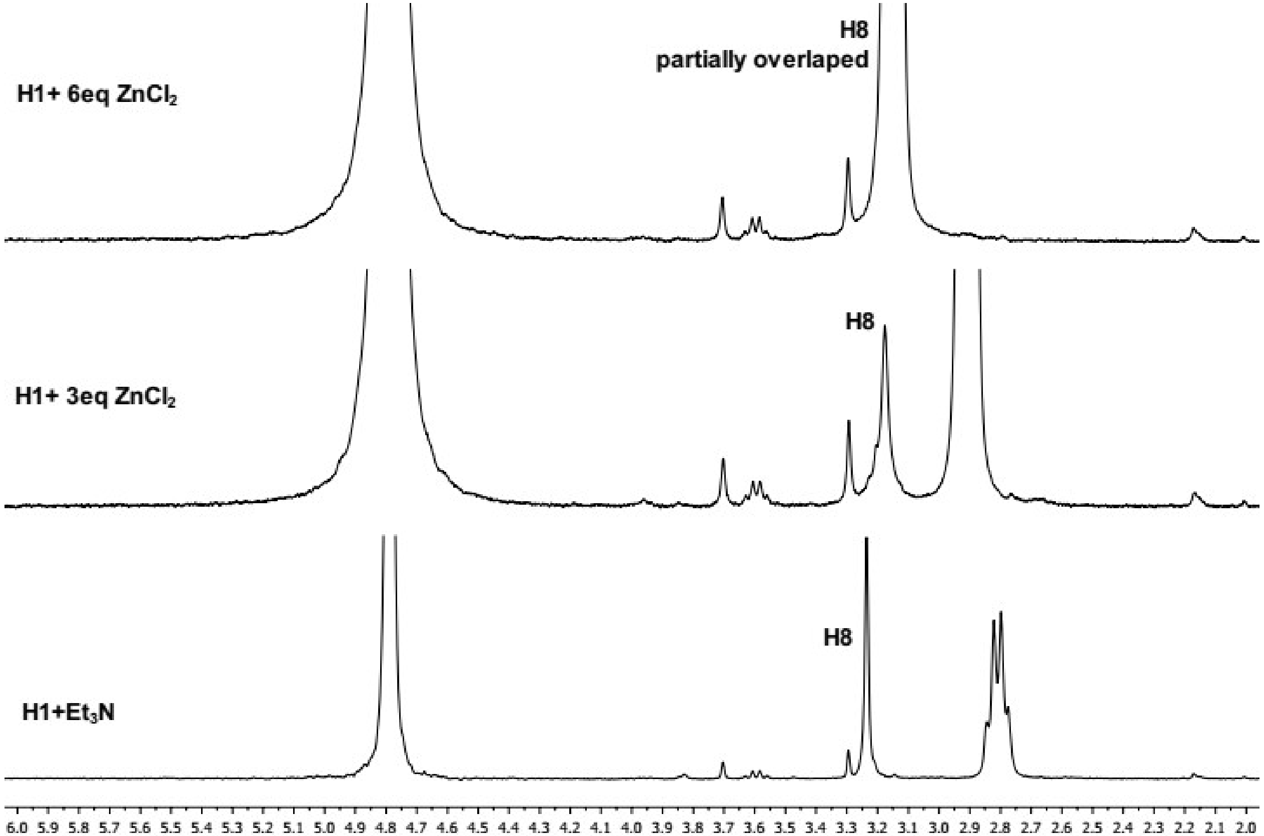


Fig. S59 ^{1}H NMR spectrum (600 MHz, D_2O) titration of solution of $\mathbf{H1}_{\mathbf{isol}}$ with $ZnCl_2$ - formation of $\mathbf{H2}_{\mathbf{in\_situ/D}}$ (aliphatic region)

S2.3.8. Route E - Synthesis of hybrid – $H3_{isol/E}$

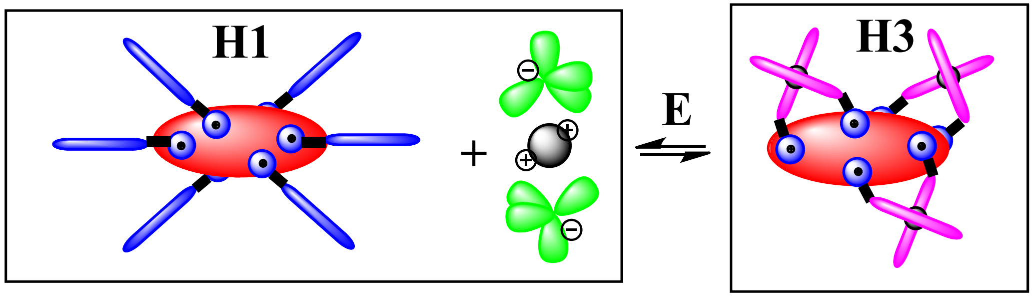


Fig. S60 Schematic representation of route E - synthesis of hybrid $\mathbf{H3}_{isol/E}$

Hybrid **H1** (15 mg; 2.45 μM) was dissolved in 5 ml of mili-Q water what resulted in a cloudy blue solution. Next, triethylamine (1.62 μl; 11.70 μM) was added (pH 8.11) and the last step was addition of zinc perchlorate hexahydrate (2.62 mg, 7.04 μM). The mixture was stirred magnetically at room temperature for 48 h to give blue coloured solution with precipitation. The final product was centrifuged (3 series of 10 minutes at 4000 rpm), what was followed by washing with water in between the cycles. Obtained product was lyophilized to give blue solid state compound. Yield: 8.04 mg, 37.84% based on hybrid **H1**.

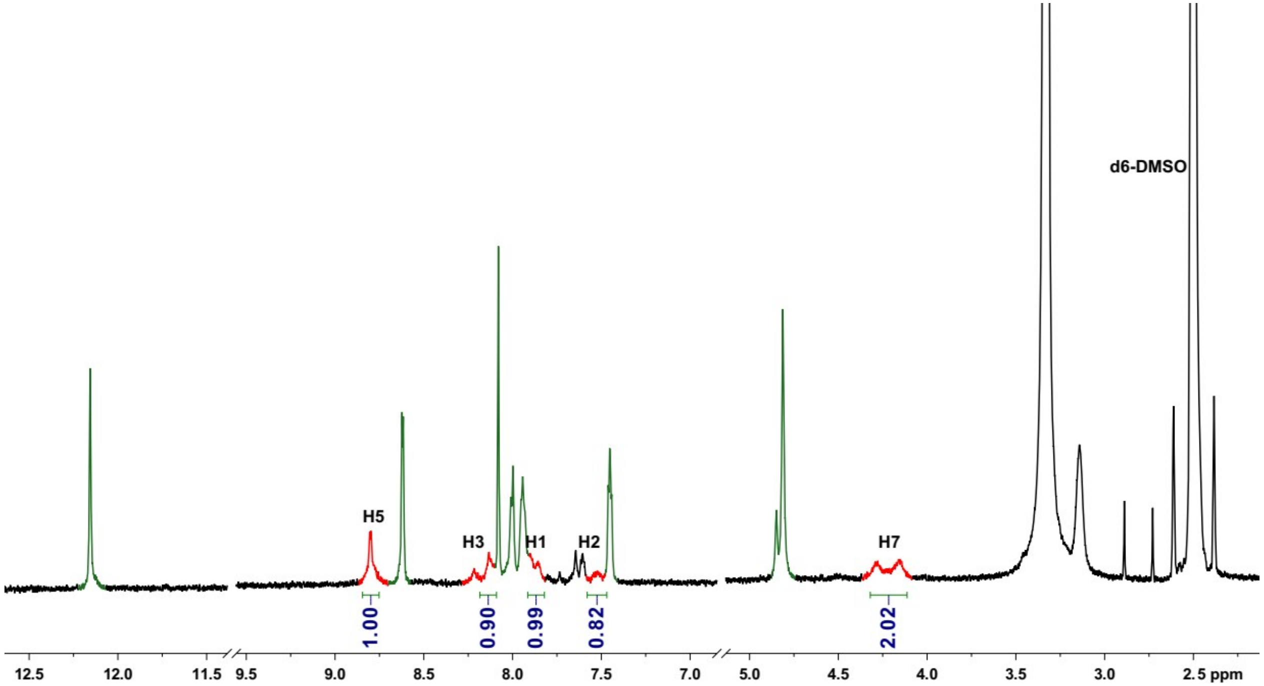


Fig. S61 ^{1}H NMR spectrum (600 MHz, *d6*-DMSO) of mixture of **H1** and **H3**$_{\mathbf{isol/E}}$, red peaks represent **H3**$_{\mathbf{isol/E}}$, green peaks represents **H1**

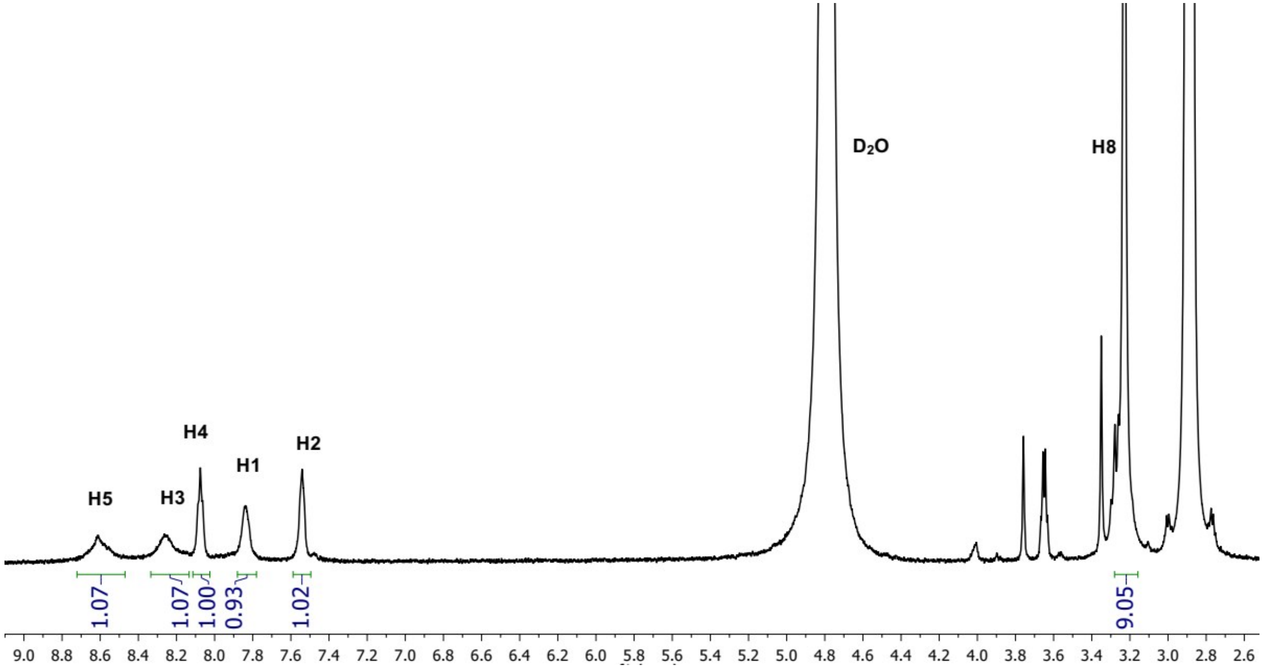


Fig. S62 ^{1}H NMR spectrum (600 MHz, D_2O) of $\mathbf{H3}_{\mathbf{in\_situ/E}}$

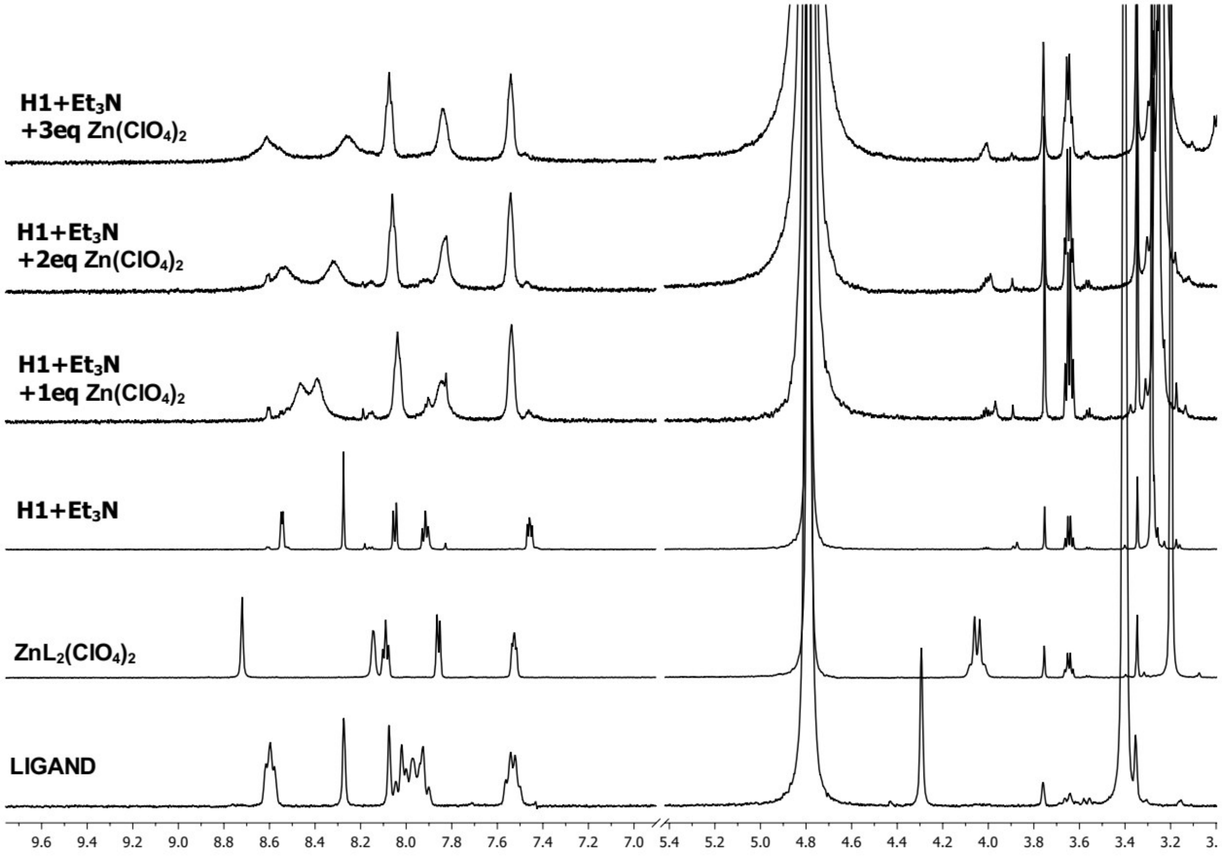


Fig. S63 ^{1}H NMR spectrum (600 MHz, D_2O) titration of complex $Zn(ClO_4)_2$ to solution of $\mathbf{H1}_{\mathbf{isol}}$ - formation of $\mathbf{H3}_{\mathit{in\_situ/E}}$

S2.3.8. Route F - Synthesis of hybrid – $H2_{isol/F}$

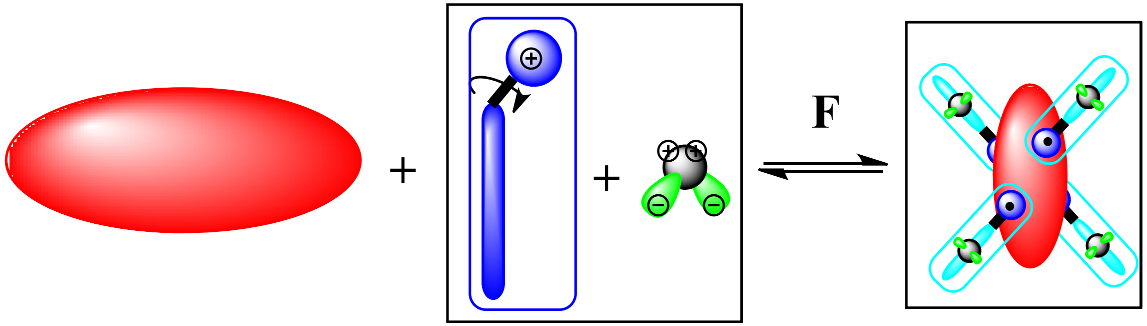


Fig. S64 Schematic representation of route F - synthesis of hybrid **$H2_{isol/F}$**

$Na_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ (94.44 mg; 19.47 μM) was dissolved in 5 ml of mili-Q water what resulted in a clear yellow solution. Next, zinc chloride (10.62mg, 77.90 μM) was added to obtain navy blue solution (pH 2.57). Then ligand L (20 mg; 77.90 μM) was dissolved in 2.5 ml of mili-Q water and triethylamine (11 μl; 77.90 μM) was added (pH 9.26). These two solutions were mixed and gave blue precipitate and blue solution (pH 6.82). The mixture was stirred magnetically at room temperature for 48 h. The final product was centrifuged (3 series of 10 minutes at 4000 rpm), what was followed by washing with water in between the cycles. Obtained product was lyophilized to give navy blue solid state compound. Yield: 87.2 mg, 85.93% based on ligand **L**.

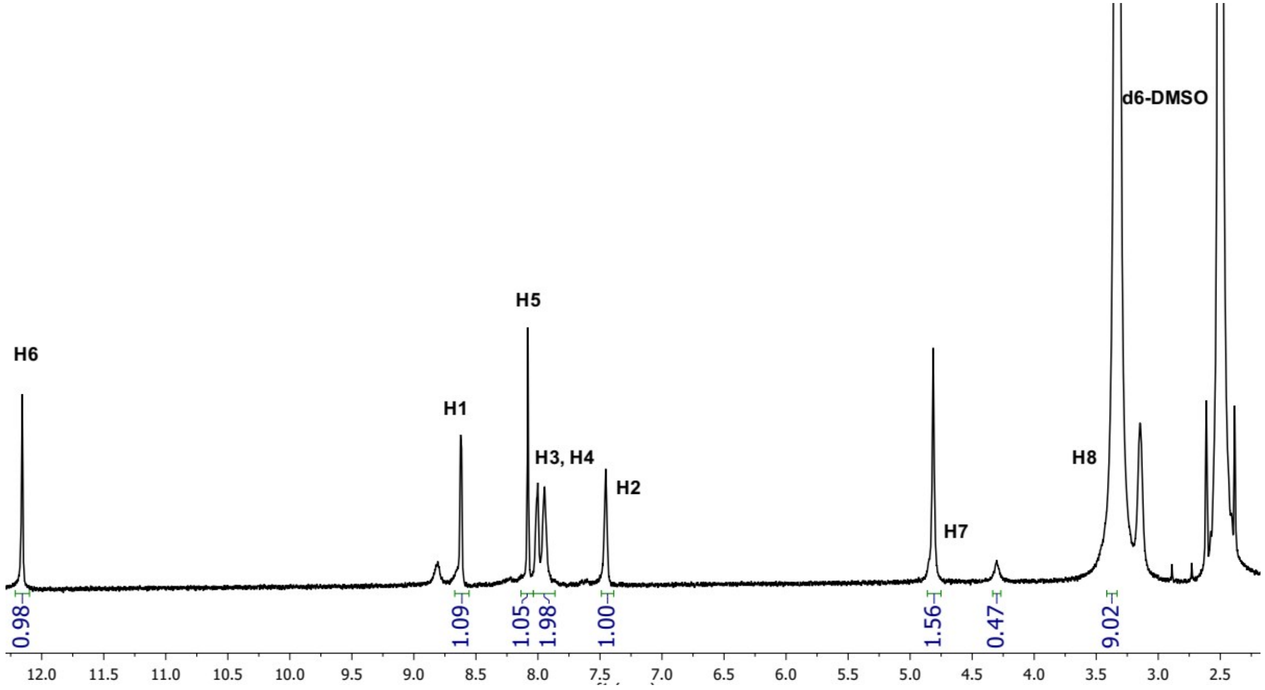


Fig. S65 ^{1}H NMR spectrum (600 MHz, *d6*-DMSO) of $\mathbf{H2}_{\mathbf{isol/F}}$

Chemical shifts the same as for **H1**, **H2** did not formed.

S2.3.9. Route G - Synthesis of hybrid – $H3_{isol/G}$

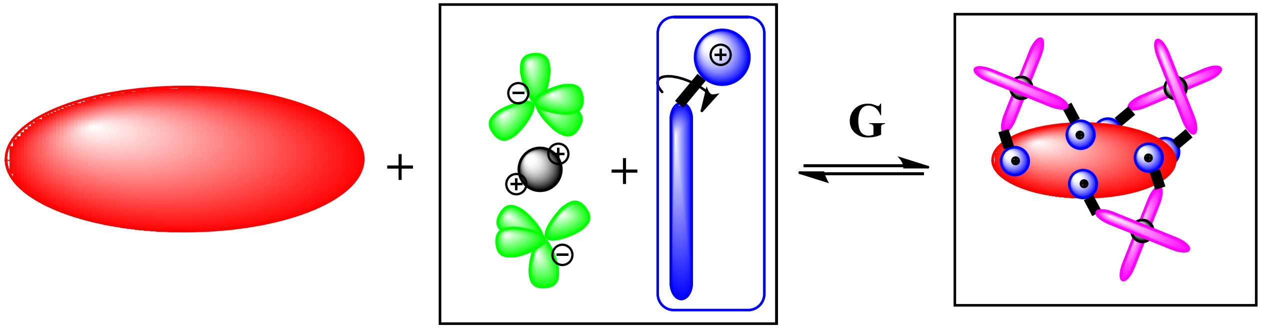


Fig. S66 Schematic representation of route G - synthesis of hybrid $\mathbf{H3}_{isol/G}$

$Na_6[\alpha\text{-}P_2W_{18}O_{62}] \cdot 14H_2O$ (75.56 mg; 15.58 μM) was dissolved in 5 ml of mili-Q water what resulted in a clear yellow solution. Next, zinc perchlorate hexahydrate (14.5 mg, 38.94 μM) was added to obtain yellow solution (pH 4.71). Then ligand **L** (20 mg; 77.90 μM) was dissolved in 2.5 ml of mili-Q water and triethylamine (11 μl; 77.90 μM) was added (pH 9.26). These two solutions were mixed and gave yellow precipitation and yellow solution (pH 5.93). The mixture was stirred magnetically at room temperature for 48 h. The final product was centrifuged (3 series of 10 minutes at 4000 rpm), what was followed by washing with water in between the cycles. Obtained product was lyophilized to give light blue solid state compound. Yield: 80 mg, 74.72% based on ligand **L**.

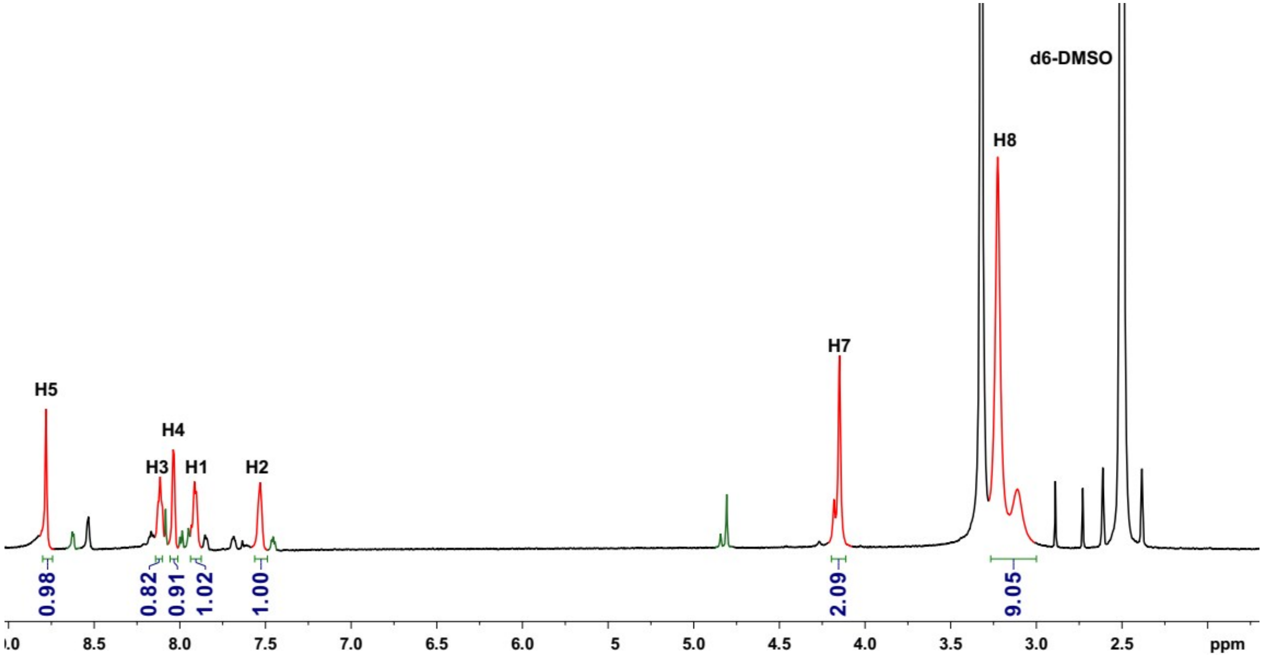


Fig. S67 ^{1}H NMR spectrum (600 MHz, *d6*-DMSO) of mixture of **H1** and **H3**$_{\mathbf{isol/G}}$, red peaks represent **H3**$_{\mathbf{isol/G}}$, green peaks represents **H1**

References

1. M. E. Reichmann, S. A. Rice, C. A. Thomas and P. Doty, *J. Am. Chem. Soc.*, 1954, **76**, 3047-3053.
2. C. R. Graham and R. G. Finke, *Inorg. Chem.*, 2008, **47**, 3679-3686.
3. W. Drożdż, A. Walczak, Y. Bessin, V. Gervais, X.-Y. Cao, J.-M. Lehn, S. Ulrich and A. R. Stefankiewicz, *Chem. Eur. J.*, 2018, **24**, 10802-10811.