Supporting information for

D4R Zinc Phosphate Cationic-Polyoxometalate Anionic Hybrids: Synthesis, Spectra, Structure and Catalytic Studies†

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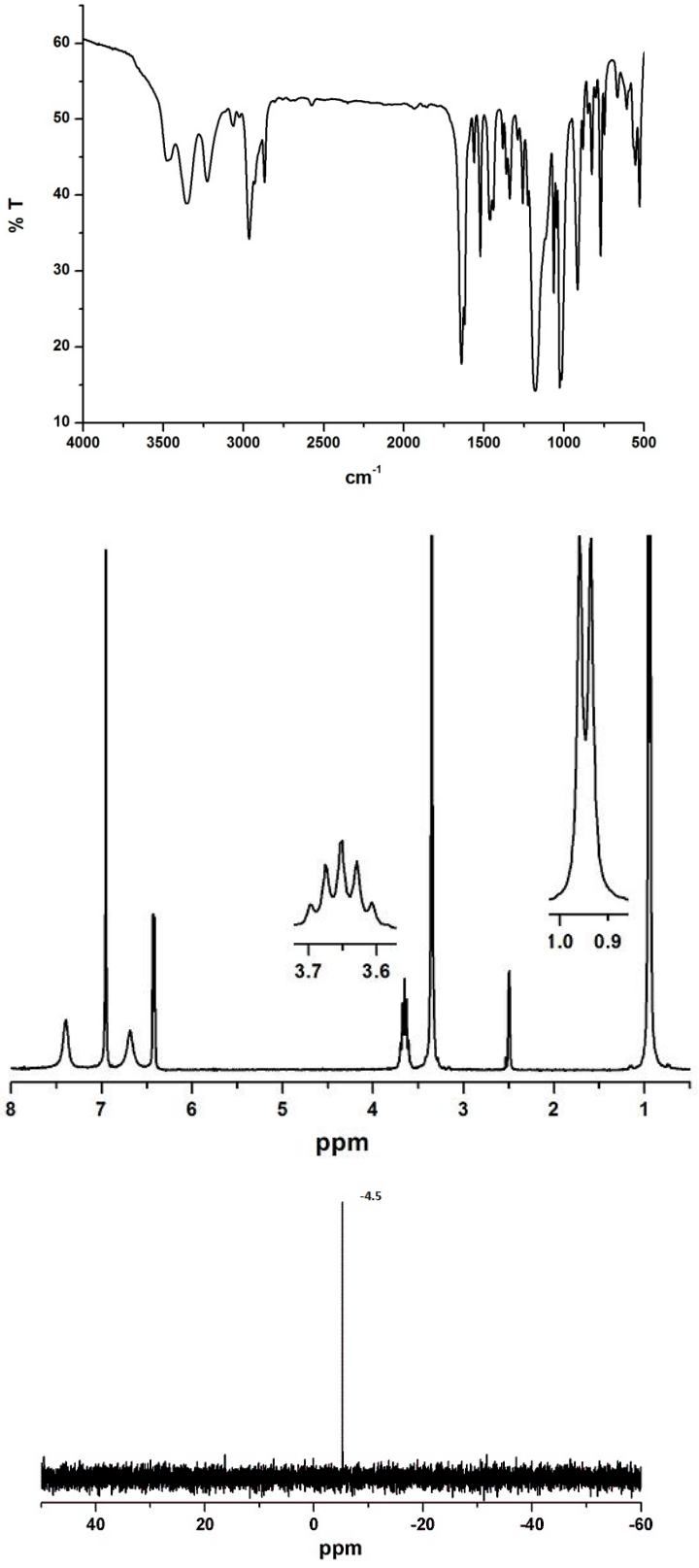

Fig. S1 FT-IR (top), ^{1}H NMR (middle) and ^{31}P NMR (bottom) spectra of [Zn(dipp)(4-ampyr]$_4$.[CH_3OH]$_4$ (**1**).

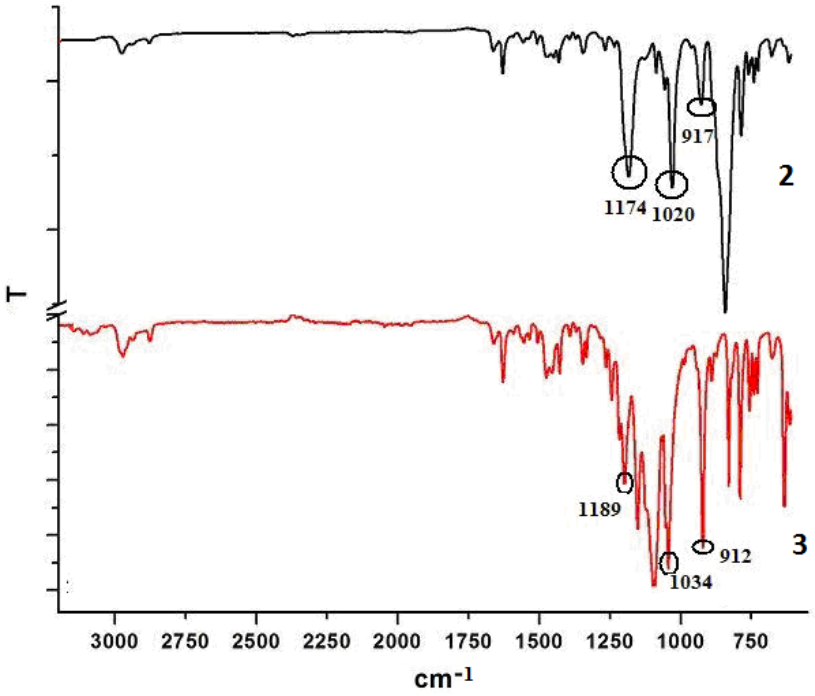

Fig. S2 IR spectra of $[Zn(dipp)(L)(X)]_4$ as neat sample, X=PF_6 (**2**) and ClO_4 (**3**).

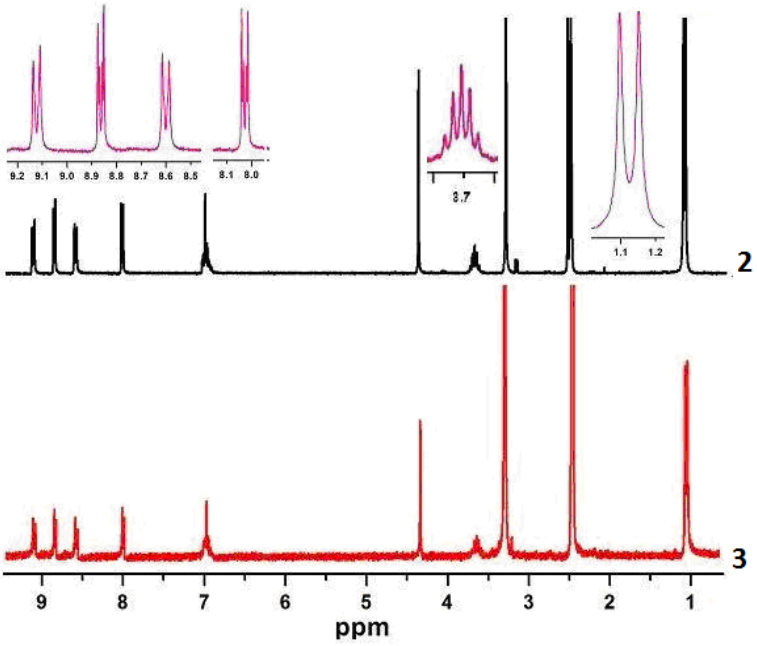

Fig. S3 ^{1}H NMR spectra of $[Zn(dipp)(L)(X)]_4$, X=PF_6 (**2**) and ClO_4 (**3**) in DMSO-d_6.

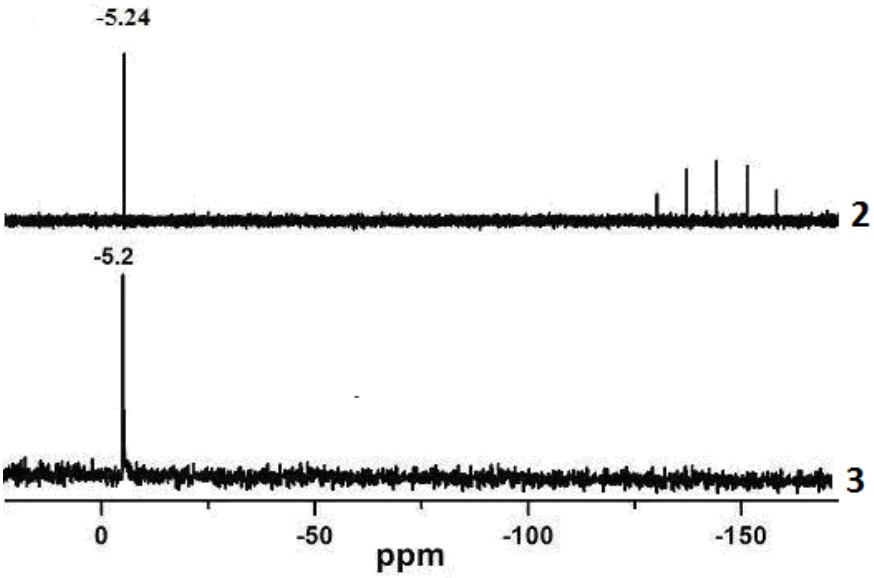

Fig. S4 ^{31}P NMR spectra of $[Zn(dipp)(L)(X)]_4$, X=PF_6 (**2**) and ClO_4 (**3**) in DMSO-d_6.

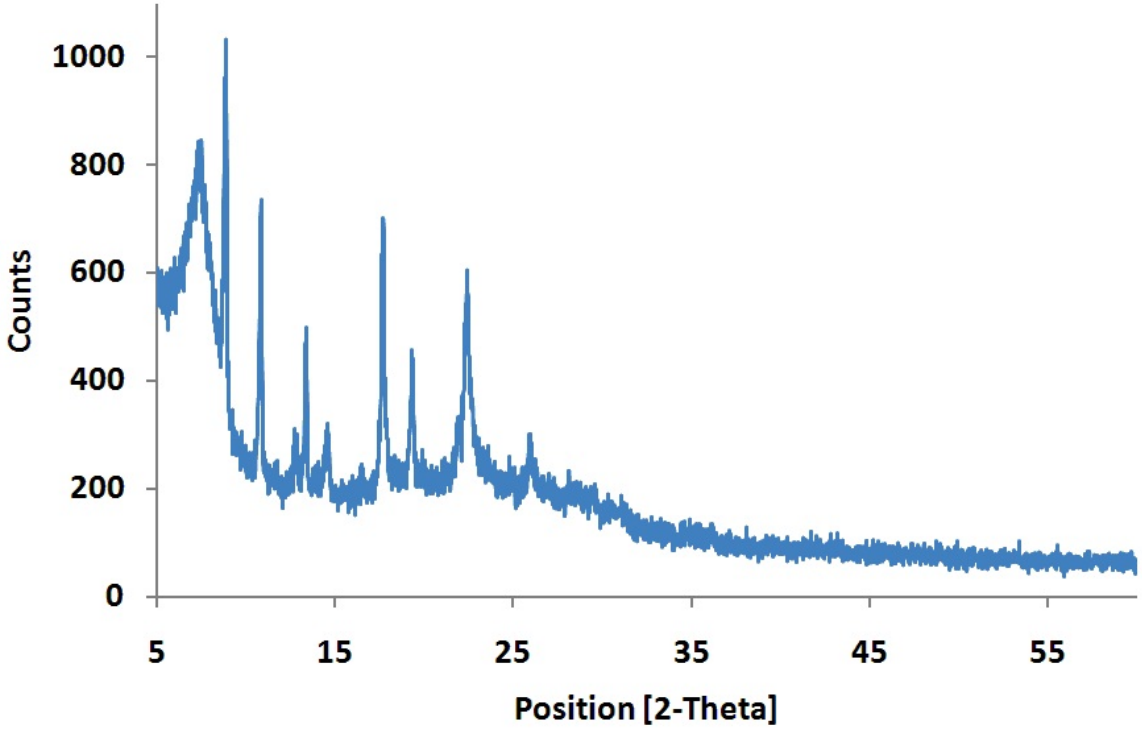

Fig. **S5** Powder XRD pattern of **2**.

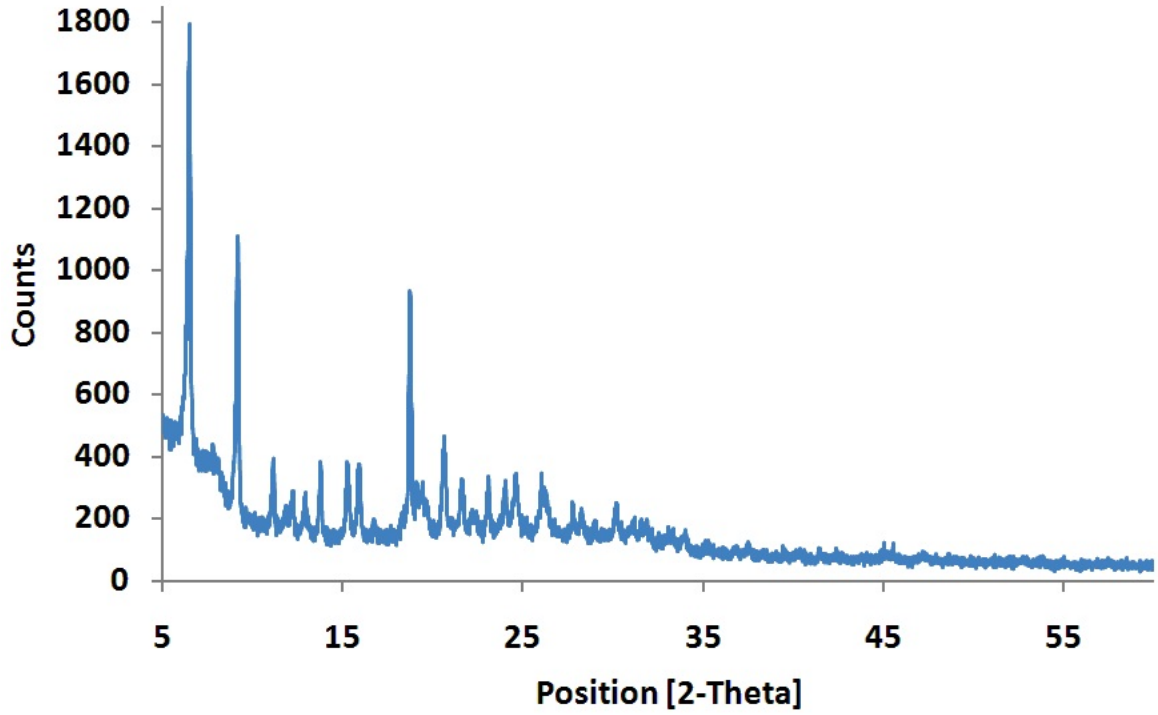

Fig. **S6** Powder XRD pattern of **3**.

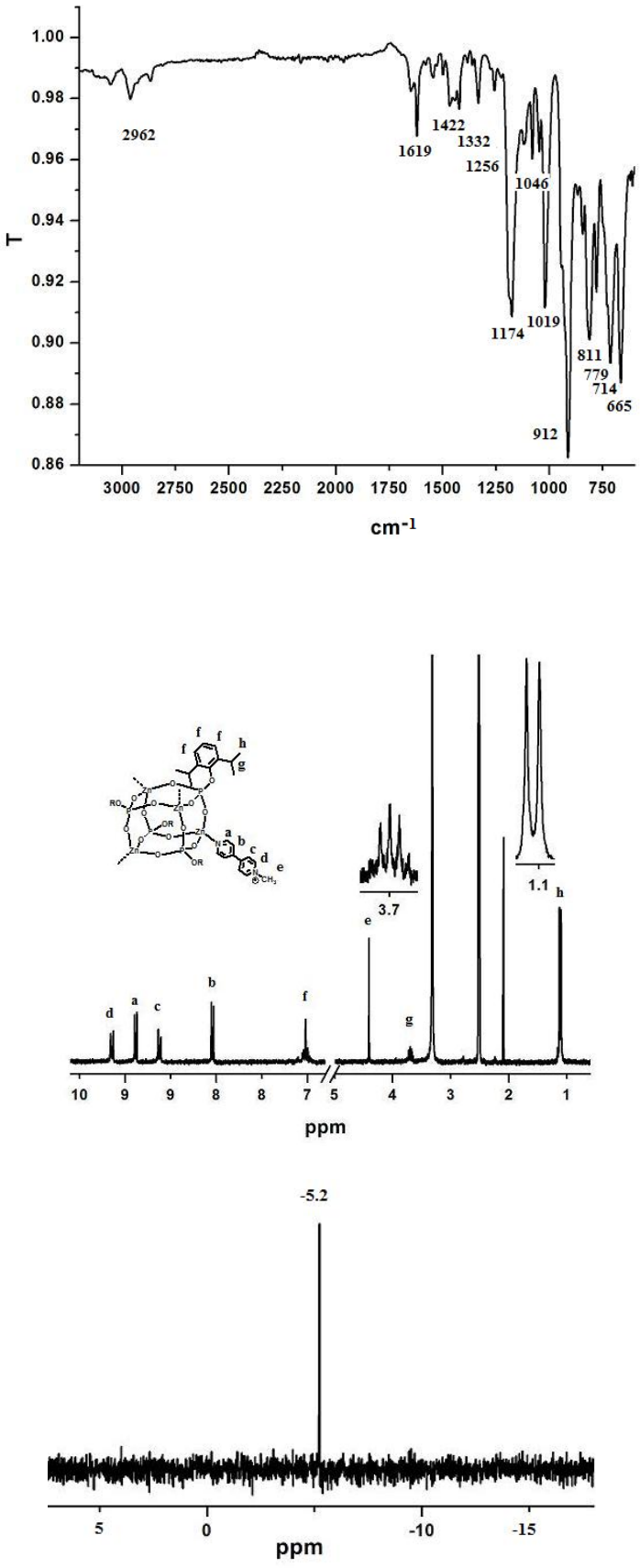

Fig. S7 FT-IR (top), ^{1}H NMR (middle) and ^{31}P NMR (bottom) spectra of hybrid **4**.

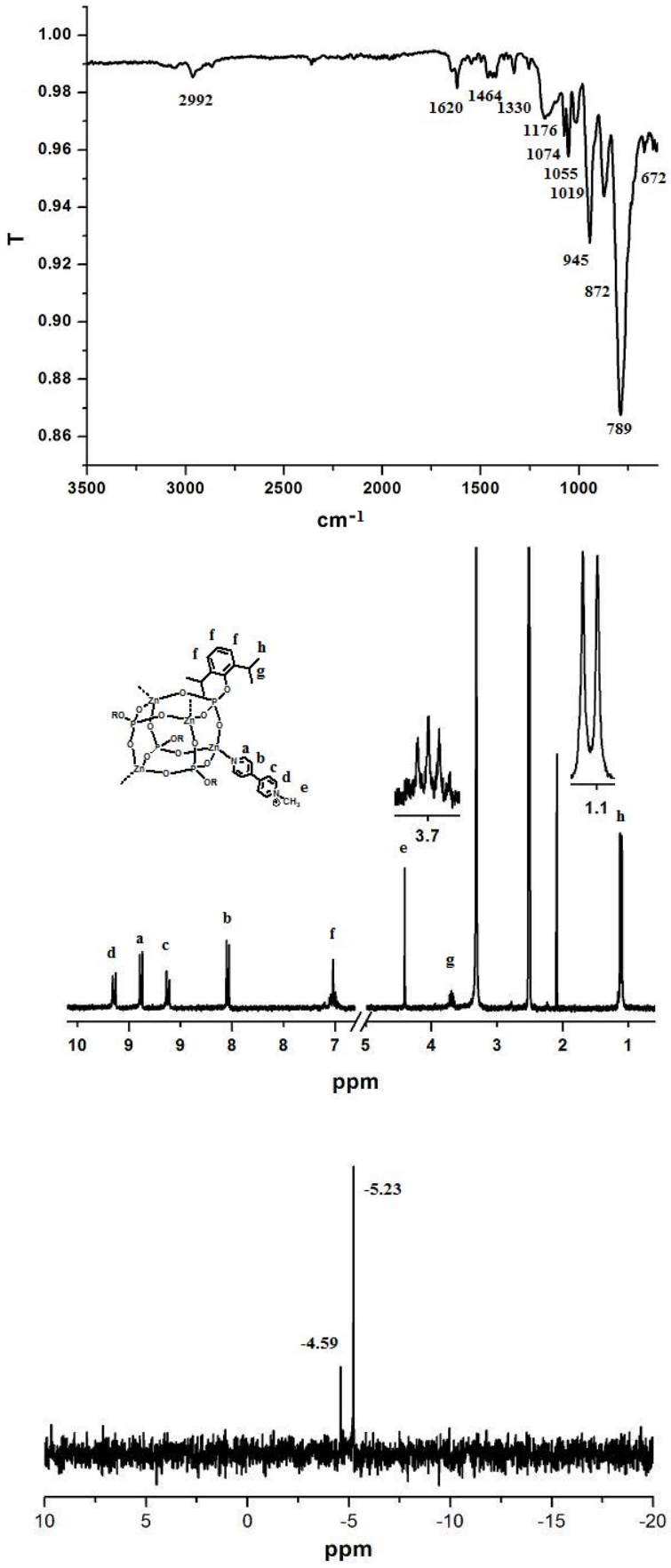

Fig. S8 FT-IR (top), ^{1}H NMR (middle) and ^{31}P NMR (bottom) spectra of hybrid **5**.

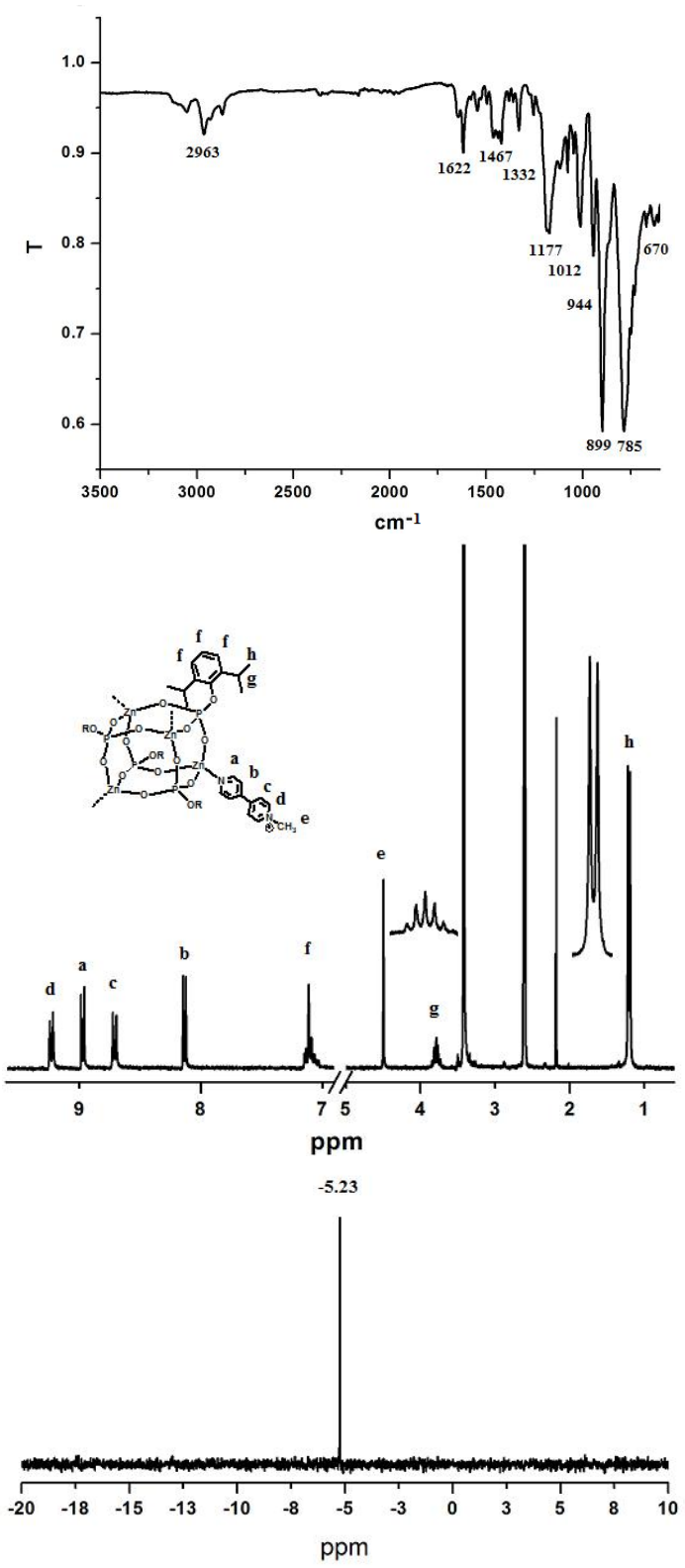

Fig. S9 FT-IR (top), ^{1}H NMR (middle) and ^{31}P NMR (top) spectra of hybrid **6**.

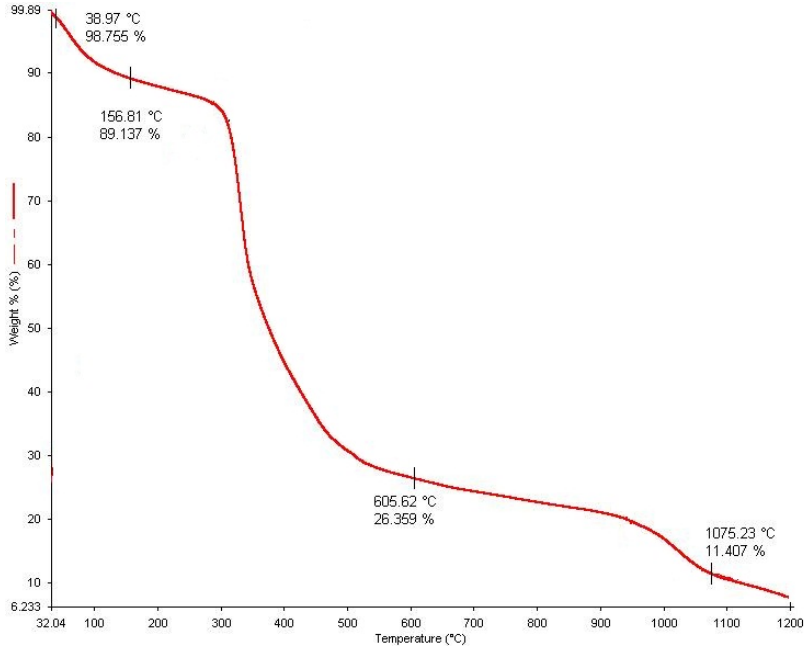

Fig. S10 TGA analyses of compound of $[Zn(dipp)(4\text{-ampyr}]_4.[CH_3OH]_4$ (**1**) under N_2 at heating rate of 10 ºC/min.

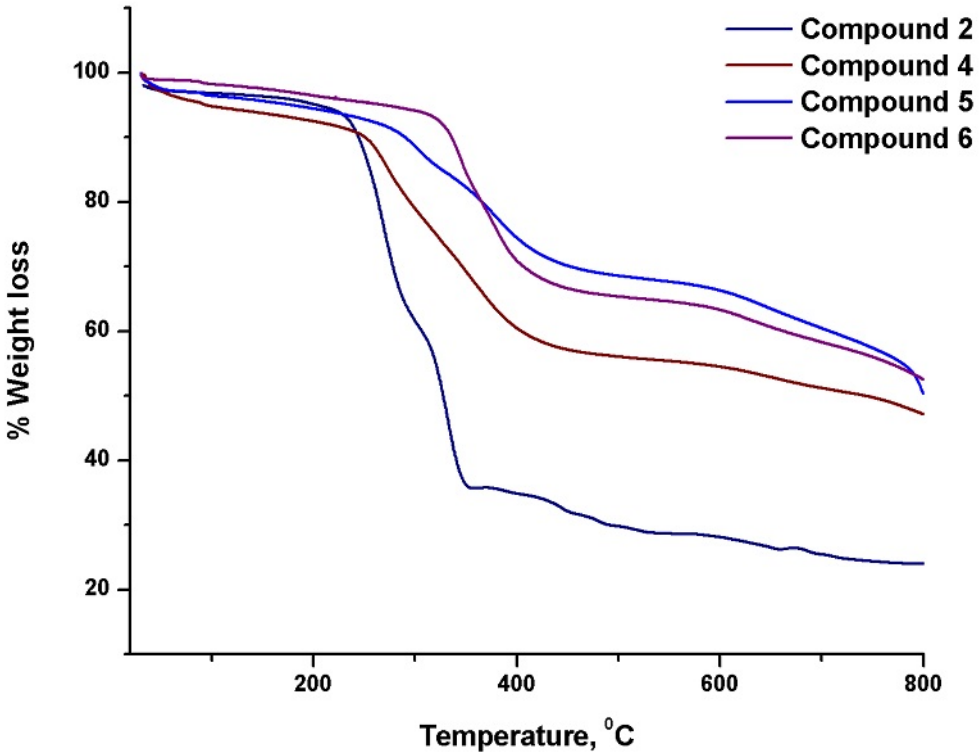

Fig. S11 TGA analyses of compound **2** and **4-6** under N_2 at heating rate of 10 ºC/min.

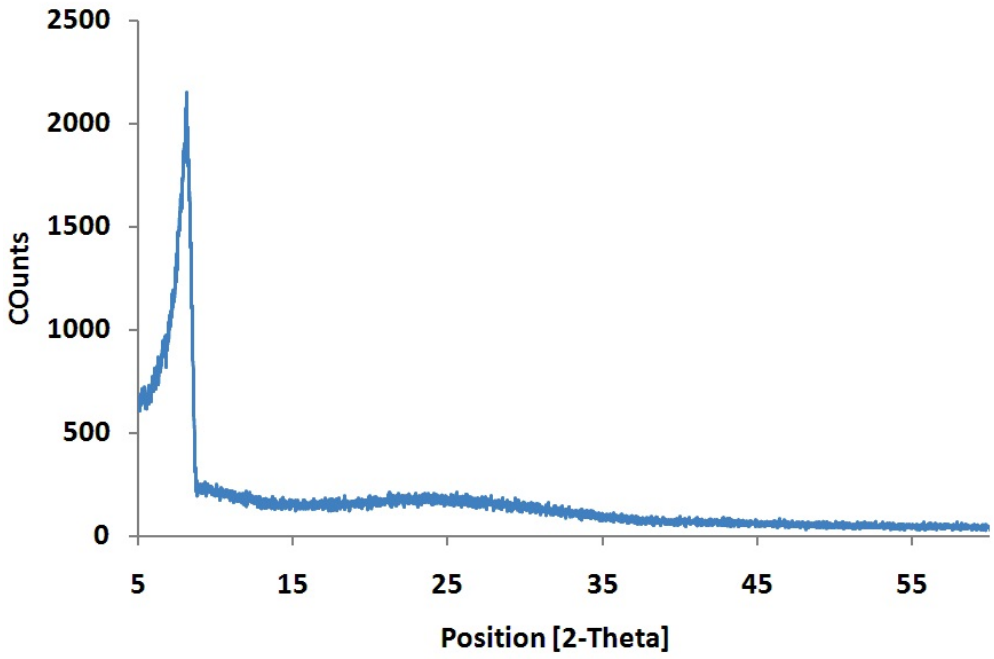

Fig. S12 Powder XRD pattern of **4**.

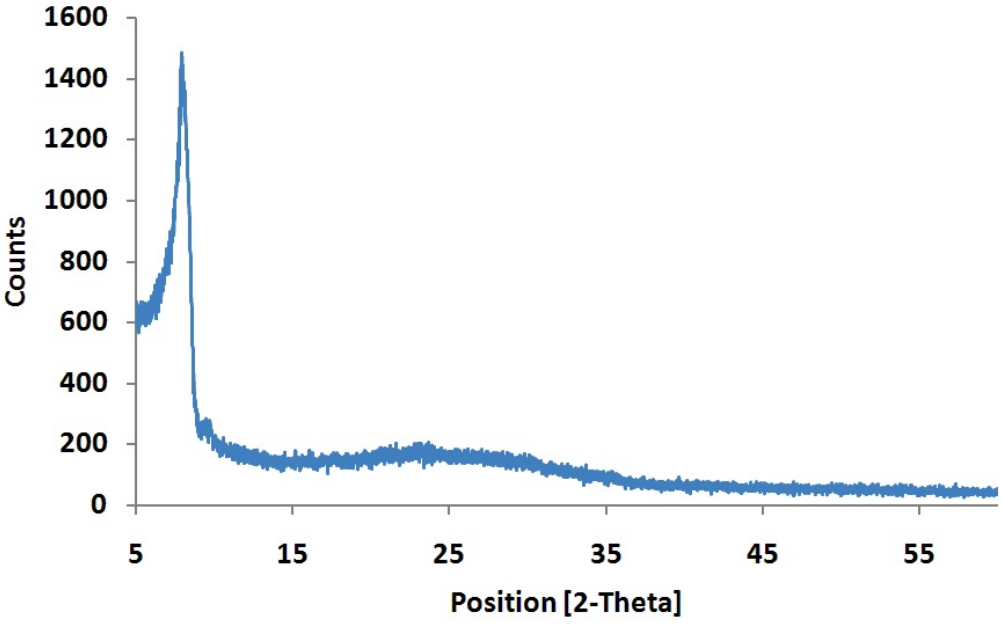

Fig. S13 Powder XRD pattern of **5**.

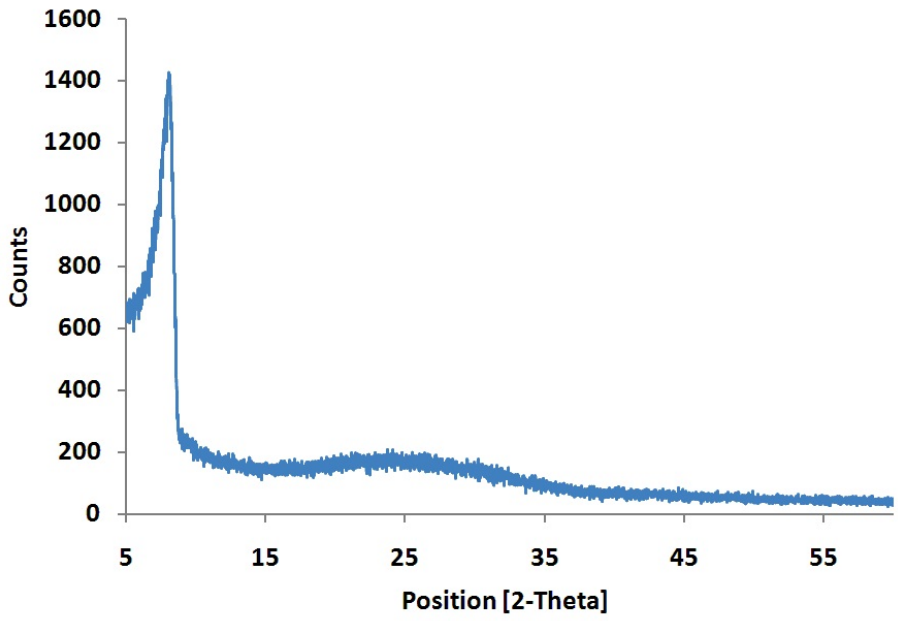

Fig. S14 Powder XRD pattern of **6**.

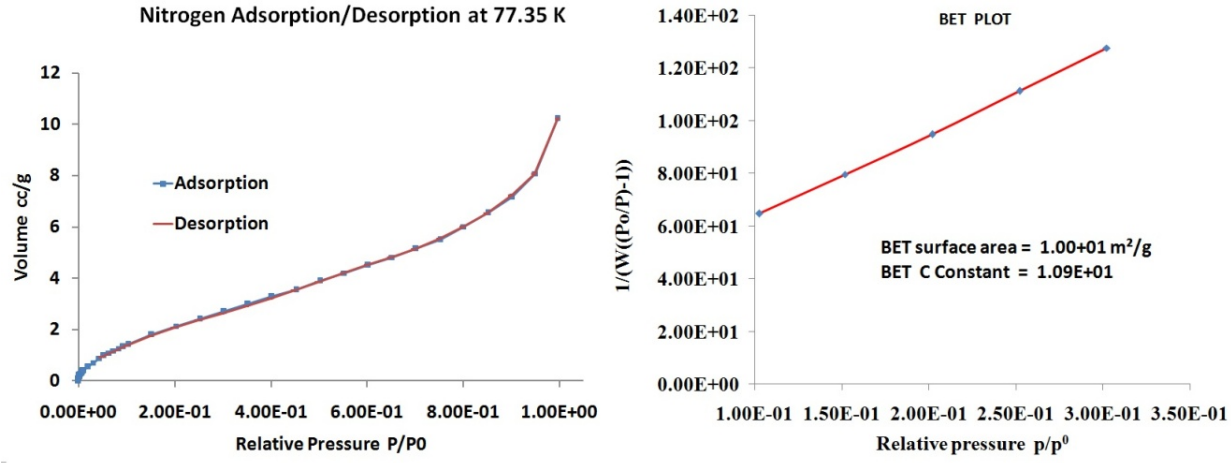

Fig. S15 Adsorption isotherm and BET plot of **4**.

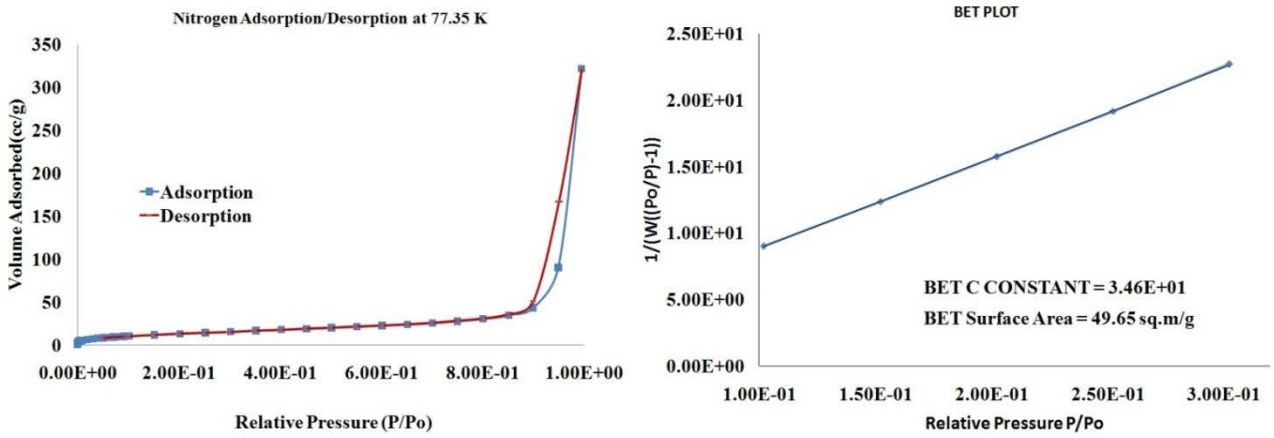

Fig. S16 Adsorption isotherm and BET plot of **5**.

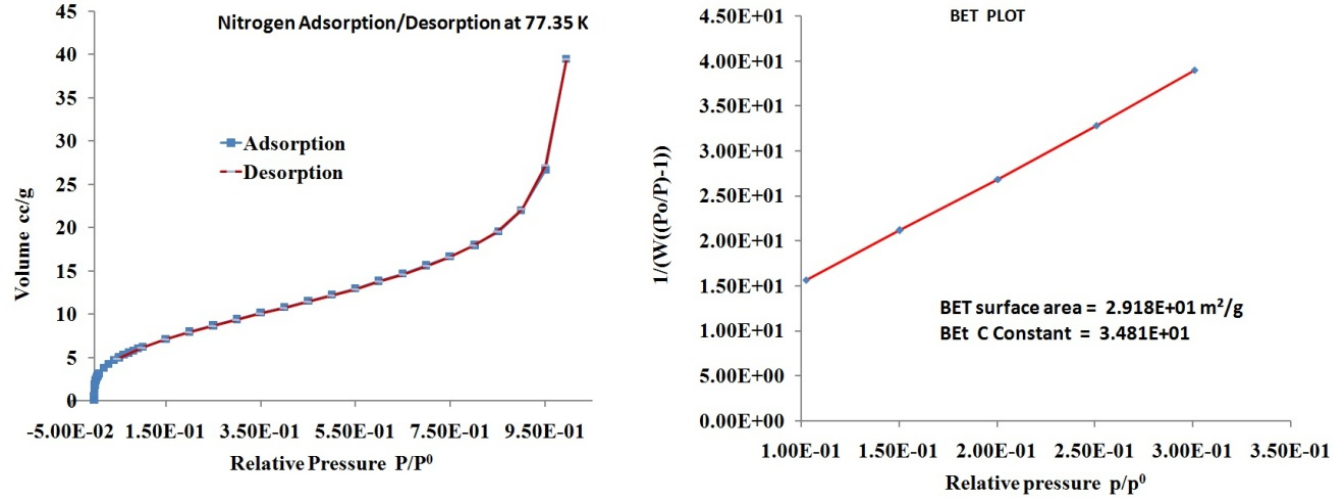

Fig. S17 Adsorption isotherm and BET plot of **6**.

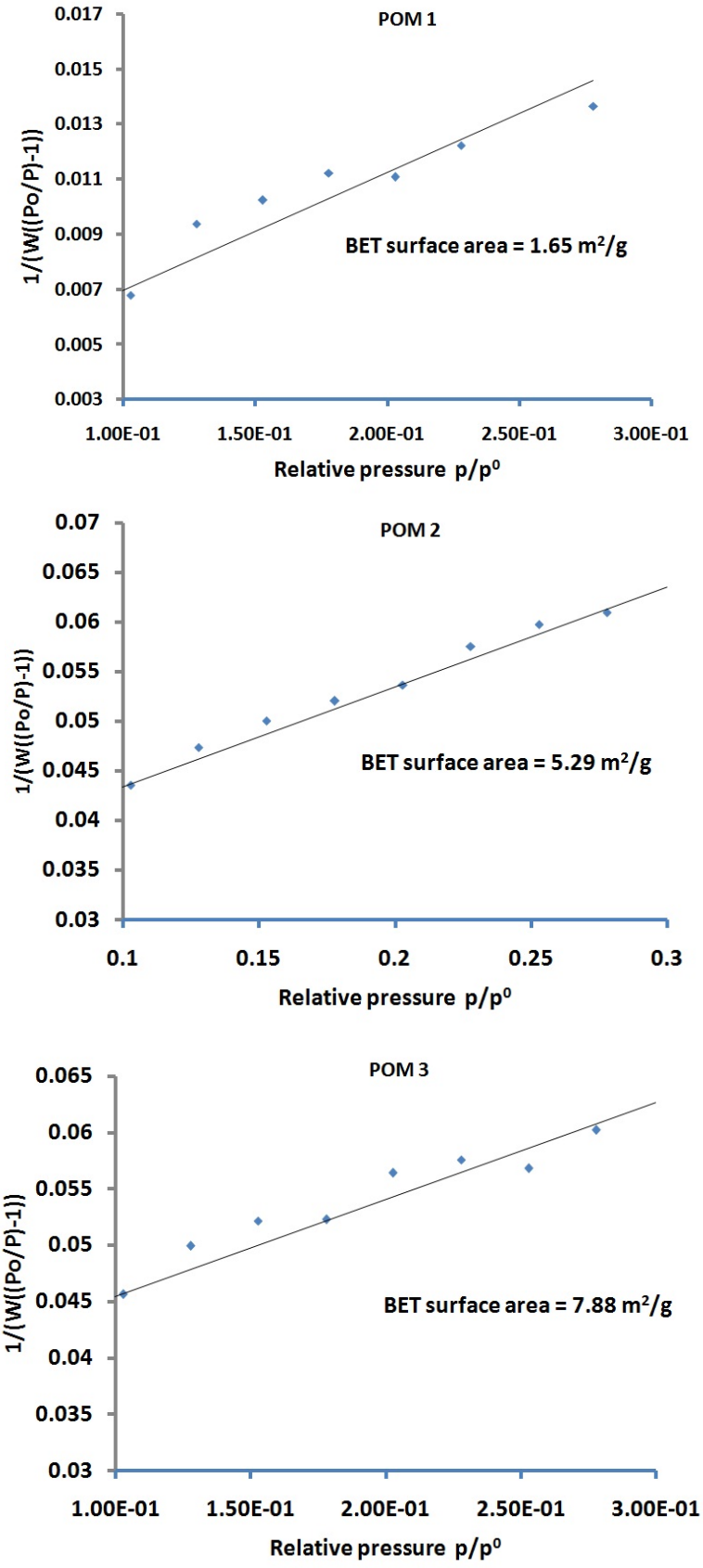

Fig. S18 BET plot of pure Polyoxometalate POM-1, POM -2 and POM-3.