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Introduction

Polyoxometalates (POMs) display a wide range of applications in diverse areas such as structural chemistry, surface chemistry, electrochemistry and catalysis.¹ High stability of POMs towards oxidizing conditions, enormously effective surface and multiple electron accepting ability have made them attractive catalysts for a variety of oxidative transformations.² The synthesis of organic–inorganic hybrid materials based on polyoxometalates (POMs) has developed into a fertile area of research due to their architecture, properties and potential in a wide range of applications.^{3,4} Hybrid POMs substituted by transition metals have found wide application in oxidative transformations with various oxygen donors.⁵ Neumann *et al.* have reported hybrid POMs prepared by mixing Q₇Na₅[WZnZn₂-

Cationic D4R zinc phosphate–anionic polyoxometalate hybrids: synthesis, spectra, structure and catalytic studies†

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A facile synthetic strategy for the generation of a new class of inorganic–organic–inorganic hybrids is reported. Replacement of labile DMSO ligands from the preformed Double-Four-Ring (D4R) zinc phosphate cluster [Zn(dipp){(CH₃)₂SO}]₄ by the addition of 4-aminopyridine (4-ampyr) results in the isolation of another discrete D4R cluster [Zn(dipp)(4-ampyr)]₄ (**1**), which forms a hydrogen-bonded framework in solid-state. If 1-methyl-4,4'-bipyridinium salts are employed instead, tetra-cationic D4R cluster [Zn(dipp)-(L)]₄[PF₆]₄ (**2**) and [Zn(dipp)(L)]₄[ClO₄]₄ (**3**) (L = 1-methyl-4,4'-bipyridinium, dipp = 2,6-di-iso-propylphenyl-phosphate) are isolated. Compound **2** was reacted with three different polyoxometalates, [TBA]₄[Mo₈O₂₆] (POM-1), [TBA]₄[PMo₁₁VO₄₀] (POM-2), and [TBA]₄[SiMo₁₂O₄₀] (POM-3) to obtain amorphous hybrids, [Zn(dipp)(L)]₄[Mo₈O₂₆] (**4**), [Zn(dipp)(L)]₄[PMo₁₁VO₄₀] (**5**), and [Zn(dipp)(L)]₄[SiMo₁₂O₄₀] (**6**), respectively. All the hybrid materials have been characterized by analytical and spectroscopic studies. The molecular structure of **1** has also been determined by single-crystal XRD measurements. N₂ gas sorption analyses show moderate BET surface area and also establish the mesoporous nature of the hybrids **4–6**. The catalytic potential of hybrids **4, 5** and **6** has been explored towards epoxidation of cyclohexene.

 $(H_2O)_2][(ZnW_9O_{34})_2]$ (Q = tetrabutylammonium) with methyl sulfate salts of tripodal polyammonium cations.⁶ These hybrid materials were found to be very effective and selective towards epoxidation of allylic alcohols and oxidation of second-ary alcohols to ketones using hydrogen peroxide as oxidant.

We have shown earlier that the reaction of $Zn(OAc)_2 \cdot 2H_2O$ with 2,6-di-iso-propylphenyldihydrogen phosphate $(dippH_2)$ in methanol produces zinc phosphate $[Zn(dipp)(CH_3OH)]_4$.^{7,8} Replacing methanol by a relatively stronger Lewis bases such as dimethylsulfoxide and subsequent structural determination led us to unambiguously establish that in solid-state these compounds posses a cubane structure, which resembles the D4R SBU of zeolitic materials. It was further established that the relatively labile dimethylsulfoxide ligands on the four zinc centres are replaceable by almost all other stronger Lewis bases belonging to the pyridine family (Chart 1).

While this substitution of DMSO/methanol ligands by functionalized pyridines and ditopic spacer ligands would be a facile synthetic route for assembling hierarchical structures, it was envisaged in this present study that this strategy could also be used for the preparation of charged (anionic/cationic) cubanes by appropriate modification of N-donor ligands used. The successful application of the strategy for assembling tetra-cationic cubanes, $[D4R]^{4+}$, and their use as precursors for the eventual preparation of [D4R][POM] hybrid structures are reported in this contribution.

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[†]Electronic supplementary information (ESI) available: FT-IR, ¹H & ³¹P NMR spectra of **1–6**, TGA and PXRD data for **2–6**. Adsorption isotherm and BET plot of **4–6** with BET plot of pure POM **1**, POM **2** and POM **3**. Crystallographic data of **1**. CCDC 917038. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50786f



Result and discussion

A. Zinc phosphate [Zn(dipp)(4-ampyr)]₄·[CH₃OH]₄ (1)

Synthesis. The reaction of $Zn(OAc)_2 \cdot 2H_2O$ with dippH₂ in solvent methanol produces [Zn(dipp)(CH₃OH)]₄.^{7,8} Addition of small amounts of dimethylsulfoxide (DMSO) to this reaction mixture however produces the tetrameric zinc phosphate, [Zn- $(dipp){(CH_3)_2SO}]_4$ (Chart 1), in view of the difference in the Lewis basicity between methanol and DMSO. Interestingly, the DMSO ligands on the zinc centres of the cubane can be further replaced by stirring a solution of [Zn(dipp){(CH₃)₂SO}]₄ with 4-aminopyridine in methanol to yield [Zn(dipp)-(4-ampyr)]₄ (Scheme 1). The product was isolated by crystallization from methanol solution and characterized by elemental analysis, spectroscopic techniques and single crystal X-ray diffraction studies. In the FT-IR spectrum, strong absorption band appearing at 1177, 1015 and 915 cm⁻¹ were due to the P=O stretching vibrations and M-O-P asymmetric and symmetric stretching vibrations respectively (Fig. S1⁺).⁷ The ¹H NMR spectrum of 1 shows well-separated peaks for all the protons of dipp and 4-aminopyridine in a 1:1 ratio. The presence of three peaks in the range 7.39-6.40 ppm correspond to the aromatic and NH₂ protons of the 4-aminopyridine ligand.



Scheme 1 Synthesis of zinc phosphate cubane species.

The peaks at 6.90 (m), 3.60 (septet) and 0.9 (d) ppm correspond to aromatic CH and CH_3 protons of the 2,6-di-iso-propylphenyl phosphate moiety (Fig. S1[†]).

Molecular structure of 1. X-Ray-quality single crystals of **1** were obtained from a methanol solution by slow evaporation of the solvent over a period of 48 h at room temperature. Single crystal X-ray structure determination reveals that the compound crystallizes in the monoclinic space group $P2_1/n$ forming a cubane like structure with four zinc and four phosphorus atoms at the alternate vertices *via* oxygen bridge.

The cubane-like core structure of **1** resembles the D4R secondary building unit and is similar to the previously reported zinc phosphate cages.⁸ A perspective view of the molecular structure of **1** is shown in Fig. 1. The observed average P–O and Zn–O distances inside the cage are 1.512 Å and 1.940 Å, respectively, while the Zn–O–P angles vary over a range of 114.8(2)°–159.9(2)°. All zinc and phosphorus atoms display tetrahedral geometry (O–Zn–O 101.2(2)–119.3(2)° and O–P–O 104.0(2)–116.1(2)°). The D4R cages are connected through intermolecular hydrogen-bonding *via* N–H protons of 4-aminopyridine, phosphate oxygen and lattice methanol molecules (Fig. 2). There are strong π – π interactions of phenyl rings as shown in Fig. 3. Seven unique intermolecular hydrogen bonds are present in the crystal structure of **1** (Table 1). The crystallographic details of **1** are given in Table 2.

B. Tetra-cationic zinc phosphate cubanes 2-3

Synthesis and spectra. The ease of substitution of DMSO from $[Zn(dipp){(CH_3)_2SO}]_4$ by 2-aminopyridine to yield 1 opens up new avenues. The four free $-NH_2$ groups on the cubane can be protonated to yield a tetra-cationic species such as $[Zn(dipp)(NC_5H_4NH_3^+)]_4$ which can be used as the cationic building block. To test this possibility, 1 was reacted with triflic acid or hydrochloric acid in methanol or DMSO to produce a clear solution (Scheme 1) which shows a single resonance in the ³¹P NMR spectrum at -7 ppm, which corresponds to the protonated form of dippH₂ ligand itself. Thus, it appears that the addition of a protic source to tetrameric



Fig. 1 Molecular structure of 1 (hydrogen atoms and solvent molecules are omitted for clarity).



Fig. 2 Schematic diagram showing hydrogen bonding network in 1 (hydrogen atoms, 2,6-di-iso-propylphenyl groups and solvent molecules are omitted for clarity).



Fig. 3 Schematic diagram showing π - π interaction in **1** (minimum distance between phenyl rings is about 3.2 Å, hydrogen atoms, 2,6-di-iso-propylphenyl groups and solvent molecules are omitted for clarity).

Table 1	Hydrogen	bonding	parameters	for	1
---------	----------	---------	------------	-----	---

D-H…A	d(D-H)	d(H…A)	$d(\mathbf{D}\cdots\mathbf{A})$	<(D–H–A)
	(Å)	(Å)	(Å)	(°)
$\begin{array}{l} N(2)-H(2W1) \cdots O(6) \\ N(4)-H(4W1) \cdots O(20) \\ N(4)-H(4W2) \cdots O(10) \\ N(6)-H(6W1) \cdots O(19) \\ N(6)-H(6W2) \cdots O(21) \\ N(8)-H(8W1) \cdots O(19) \\ N(8)-H(8W2) \cdots O(12) \end{array}$	$\begin{array}{c} 0.842(5)\\ 0.942(5)\\ 0.908(4)\\ 0.894(5)\\ 0.975(6)\\ 1.102(6)\\ 1.158(6) \end{array}$	$\begin{array}{c} 2.176(3)\\ 2.006(6)\\ 2.209(4)\\ 2.081(4)\\ 2.331(1)\\ 2.169(4)\\ 1.911(3)\end{array}$	2.986(6) 2.948(7) 3.055(6) 2.925(6) 3.232(2) 3.037(7) 3.022(7)	$161.6(4) \\178.9(4) \\154.8(4) \\157.0(5) \\153.4(4) \\133.7(3) \\159.2(3)$

cluster 1 not necessarily protonates the cluster but completely destroys it, producing the protonated ligand $[H-dippH_2]^+$, along with concomitant formation of either zinc triflate or zinc chloride, respectively. Hence an alternate design for generation of cationic D4R cluster was envisaged.

Table	2	Curvetel	1 - + -	£	
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Compound	$[Zn(dipp)(4-ampyr)]_4(CH_3OH)_3(1)$		
Formula	$C_{71}H_{92}N_8O_{20}P_4Zn_4$		
Formula weight	1762.89		
Temperature/K	293(2)		
Wavelength/Å	0.71073		
Crystal system	Monoclinic		
Space group	P21/n		
a/Å	17.174(4)		
<i>b</i> /Å	22.619(4)		
c/Å	22.403(5)		
$\alpha / ^{\circ}$	90		
$\beta/^{\circ}$	103.887(2)		
$\gamma/^{\circ}$	90		
Volume/Å ³	8447.8(3)		
Ζ	4		
Density (calculated)/Mg m^{-3}	1.386		
Absorption coefficient/mm ⁻¹	1.267		
F(000)	3656		
Reflections collected	61 274		
R _{int}	0.0359		
Data/restraints/parameters	14 834/1/964		
Goodness-of-fit on F^2	1.066		
$R_1, WR_2 \left[I > 2\sigma(I) \right]$	0.0560, 0.1636		
R_1 , w R_2 (all data)	0.0861, 0.1732		

An easier way of introducing the cationic centers on the cubane would be to use pyridine ligands that already bear a positive charge. One of the most well studied compounds belonging to this class of ligands is mono-N-methylviologen. The ruthenium and other organometallic complexes of N-methyl viologen have been well studied in the literature.⁹ Hence the reaction of [Zn(dipp){(CH₃)₂SO}]₄ with 1-methyl-(4,4'-bipyridinium) salts were investigated instead of 4-aminopyridine as described above. Thus stirring a solution of $[Zn(dipp){(CH_3)_2SO}]_4$ with 1-methyl-4,4'-bipyridinium salts (Scheme 2) in methanol at room temperature yield tetra-cationic species $[Zn(dipp)(L)]_4[PF_6]_4$ (2) and $[Zn(dipp)(L)]_4[ClO_4]_4$ (3). The isolated compounds 2 and 3 are air and moisture stable and are soluble in polar solvents. These tetra-cationic zinc phosphate cubanes were characterized by elemental analysis, FT-IR, ¹H and ³¹P NMR spectroscopic methods and also analyzed by PXRD studies. The elemental analysis values obtained for these compounds support the chemical formulation $[Zn(dipp)(L)]_4X_4$ (X = PF₆ and ClO₄).

The IR spectrum shows strong absorption at 1174 cm^{-1} for 2 and 1189 cm^{-1} for 3 due to the P=O stretching vibrations. Bands at 1020 and 917 cm⁻¹ for 2 and 1034 and 912 cm⁻¹ for



Scheme 2 Synthesis of tetra-cationic species 2 and 3

Paper





Fig. 4 1 H NMR spectra of [Zn(dipp)(L)]₄[X]₄, X = PF₆ (2) and ClO₄ (3) in DMSO-d₆.

3 were due to the M–O–P asymmetric and symmetric stretching vibrations (Fig. S2 \dagger).⁷ The absence of any absorptions at around 2350 cm⁻¹ indicates that there is no P–OH group of the phosphate ligand left in the complexes.

The ¹H NMR spectrum of 2 shows well separated peaks for all the protons of dipp and 1-methyl-4,4'-bipyridinium units in a 1:1 ratio. The presence of four doublets in the range 9.1-8.0 ppm and a singlet at 4.3 ppm corresponds to the aromatic and methyl protons of 1-methyl-4,4'-bipyridinium ligand. Similarly the appearance of peaks at 6.9 (m), 3.6 (septet) and 1.1 (d) ppm correspond to aromatic, -CH and -CH₃ protons of 2,6-di-iso-propylphenylphosphate moiety (Fig.4 and S3⁺). In the ³¹P NMR spectrum of 2, a singlet is observed at -5.2 ppm corresponding to the phosphorous of the dipp phosphate ligand, while the observed septet centered at -144 ppm arises out of the PF₆ anion (Fig. S4⁺). The relative integration of these two sets of peak indeed reveals that the DMSO ligands have been quantitatively replaced by mono-Nmethylviologen ligand. The ¹H and ³¹P NMR spectra of 3 also show similar spectral characteristics (Fig. S3 and S4⁺). The high crystalline nature of these tetra-cationic materials were confirmed by PXRD studies (Fig. S5 and S6⁺). These compounds with exo-cubane cation centers can readily serve as ideal starting material for the synthesis of inorganic-organic-POM hybrid materials.

C. Syntheses of hybrid materials 4-6

Synthesis. The D4R–POM hybrid compounds **4–6** are readily prepared by stirring a solution of **2** in acetonitrile with an acetonitrile solution of POMs (Scheme 3). Compounds **4–6** can also be obtained starting from **3** instead of **2**. In a typical reaction, stirring the reaction mixture for a few hours results in the precipitation of the desired hybrid polyoxometalate. The elemental analysis values obtained for all the hybrid

compounds indicate the elimination of NR₄PF₆ or [TBA]PF₆ from the reaction to yield [D4R]⁴⁺[POM]⁴⁻ hybrids. Minor deviations observed in the found carbon values of **5** and **6** (see Experimental) are probably due to any small deviations in the 1:1 stoichiometry of the hybrids or the presence of TBA·PF₆ within the pores of hybrids (repeated washing of the hybrids with methanol did not substantially improve the observed values).

Spectra. The FT-IR spectrum of **4** shows strong bands at 1174, 1019 and 912 cm⁻¹, which correspond to the P=O vibrations and M-O-P asymmetric and symmetric stretching vibrations (Fig. S7†).⁷ The ¹H NMR spectrum of **4** shows well separated peaks for the zinc cubane which are similar to compound **2** except for the peaks due to the TBA protons (Fig. 5). As expected, the ³¹P NMR spectrum shows no peak in the region of –144 ppm, suggesting the complete replacement of PF₆⁻ anions by POM anions in compound **4** (Fig. S7†). The ¹H and ³¹P NMR spectra of **5** and **6** show a similar pattern to those of **4** (Fig. 5 and Fig. S8 and S9†). The ³¹P NMR spectrum of **5** is particularly revealing since PO₄ moieties are available both in



Fig. 5 ¹H NMR and ³¹P NMR spectra of 2 and 4–6 in DMSO-d₆.



Fig. 6 TGA profiles of 2 and hybrids 4--6 under N_2 at heating rate of 10 $^\circ\text{C}\ \text{min}^{-1}.$

[POM] and [D4R] parts in a 1:4 ratio in the hybrids; as expected two single resonances in a 1:4 ratio appear at -4.5 and -5.2 ppm. This observation clearly provides further convincing evidence for the formation of 1:1 D4R–POM hybrids in these systems where the cationic and anionic parts are separated by the "MeQ" spacers which probably results in a porous structure (*vide infra*).

TGA studies. Thermal behaviour of 1-6 has been investigated in the temperature range 25-800 °C under a stream of nitrogen gas. The TGA profiles of the tetra-cationic D4R cubane 2 along with those of the hybrids 4-6 are shown in Fig. 6. The most striking feature of Fig. 6 is the significant enhancement in the thermal stability of hybrids 4-6 compared to cubane 2. Barring the loss of any solvent molecules such as methanol and occluded water from the porous structure, the new hybrid structures are stable until 310-350 °C whereas the decomposition of 2 sets in even before 250 °C. For the D4R cubane 2, a three step weight loss corresponding to the loss of 77% of the total weight of the sample results in the residual mass of 23%. This corresponds to the formation of $Zn_2P_2O_7$, which is consistent with the thermal decomposition product of zinc di-tert-butylphosphate complexes reported by us earlier.¹⁰ In the case of hybrids 4-6, the single step weight loss corresponds to the loss of organic groups from the D4R tetracation amounting to roughly 40% of the total mass.

Morphology and porosity. The morphology of the hybrids have been established by electron microscopy. Fig. 7 (plate A) shows that the hybrid **4** exists as plates which grown to some extent in an irregular fashion. Compound **5** (plate B) forms spherical nano-islands with granule size of about 30-40 nm. Compound **6** (plate C) forms plates of nearly 200 nm size with spherical nano-island spreading in between the plates. It is evident from the SEM analyses that hybrid compounds have smaller grain size and hence are amorphous in nature **6** (C). Powder X-ray diffraction pattern of these compounds further supports the highly amorphous nature of all the three hybrids





Fig. 7 SEM images of hybrid 4 (A), 5 (B) and 6 (C).

(Fig. S12–S14^{\dagger}), as has been observed for other organic-inorganic hybrid polyoxometalates.⁶

Gas adsorption measurements were performed on parent POMs (POM-1 to POM-3) as well as the hybrids 4-6 to assess the effect of hybrid formation on surface area and porosity. The N₂ gas adsorption measurements were performed at 77 K after drying the as synthesized samples under a dynamic vacuum at 100 °C to remove any guest molecules. The BET surface area of 4, 5, and 6 were found to be 10.0, 49.6 and 29.1 m² g⁻¹, while those of the corresponding parent TBA-POMs were found to be only 1.6, 5.2, and 7.8 m^2 g⁻¹, respectively. From the measured multipoint adsorption isotherms, the pore diameters were derived by assuming cylindrical pore geometry and their average values were found to be 6.3, 40.0, and 8.0 nm for hybrids 4, 5, and 6, respectively. Fig. 8 shows the adsorption isotherm for 5, which is characteristic of mesoporous solids where the rapid adsorption takes place at P/P^{o} values of 0.95.11 The mesoporous nature of the hybrids, albeit with moderate surface area, is responsible for the high catalytic activity of these hybrids (vide infra). For comparison, the organic-inorganic hybrids employed by Neumann et al., $[\{WZnZn_{2}(H_{2}O)_{2}\}\{(ZnW_{9}O_{34})_{2}\}][Y]_{4} (Y = tripodal poly$ ammonium cation), showed a similar surface area (27 and 51 m² g⁻¹) but were also found to be mesoporous with average pore diameter of 3.6 nm.^{6a}

Catalytic studies. The utility of polyoxometalates as oxidation catalysts has been well established in the literature. However, the as synthesised polyoxometalates are non-porous solids showing very low surface area (*vide supra*; $1-8 \text{ m}^2 \text{ g}^{-1}$ for the pure POMs used in this study). Mesoporous hybrid materials such as compounds **4–6**, on the other hand, are good heterogeneous catalysts for oxidation reactions in the presence of hydrogen peroxide (Scheme 4).¹² Hence we have carried out

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Fig. 8 $\,N_2$ adsorption isotherm and BET plot (inset) of 5 (blue – N_2 adsorption and red – N_2 desorption).



Scheme 4 Epoxidation of cyclohexene.

epoxidation of cyclohexene to establish the superior activity of the three hybrid polyoxometalates over the parent POMs themselves.

Thus two sets of epoxidation reactions were carried out; one set with POM-1, POM-2, and POM-3, and the other set with hybrid-1, hybrid-2, and hybrid-3. In order to check any effect the D4R zinc phosphate could have in the catalysis, a plain catalytic run with 2 as the only catalytic component was also carried out. All the epoxidation reactions have been performed under the following conditions: 0.2 mmol cyclohexene, 5 mL (30%) H_2O_2 , 0.035 mmol catalyst; reaction temperature 85 °C. The products obtained were monitored by GC measurements.

As expected, the cationic component of the hybrids, namely the D4R cubane, is totally inactive showing no formation of epoxide even after 8 hours (Table 3, entry 1; Fig. 9). The three pure POMs show 80, 77, and 90% of epoxide formation in 8 hours at the conditions mentioned above. Switching from

 Table 3
 Cyclohexene epoxidation by D4R cubane, pure POMs and hybrids

Catalyst	Time (h)	Epoxide (%)
Tetra-cationic-D4R cubane		
$[Zn(dipp)(L)]_4[PF_6]_4(2)$	8	0
Pure POMs		
$[TBA]_4[MO_8O_{26}]$ (POM-1)	8	80
$[TBA]_4[PMO_{11}VO_{40}]$ (POM-2)	8	77
$[TBA]_4[SiMo_{12}O_{40}] (POM-3)$	3	89
D4R–POM hybrids		
$[Zn(dipp)(L)]_4[Mo_8O_{26}](4)$	6	90
$[Zn(dipp)(L)]_4[PMO_{11}VO_{40}](5)$	8	89
$[Zn(dipp)(L)]_4[SiMo_{12}O_{40}](6)$	5	100



Fig. 9 Diagram shows the efficiency of different catalysts for epoxidation of cyclohexene.

these simple non-porous TBA-POMs to mesoporous hybrids **4–6** increases the epoxide yields at least by 10% in each case, achieving a yield of 100% for catalyst **6** within 5 hours (Table 3). The silico-molybdate anion is catalytically more efficient both in non-porous pure and mesoporous hybrid forms (89 and 100% conversion to epoxide respectively). Although the porosity of the hybrid material increases the catalytic activity, the relative efficiency of the POM anions remain unaffected by the hybrid formation (*e.g.* **5** is more porous than **6**, but still **6** is more active because its parent POM is more active).

Conclusion

A new strategy of using D4R zinc phosphates as counter cations in hybrid polyoxometalate chemistry has been demonstrated for the first time. Neutral D4R cubane, [Zn(dipp)-(4-ampyr)]₄, originally prepared for this purpose did not undergo clean protonation reaction at the 4-amino position and instead led to the demetallation of the D4R cubane. Change of N-donor ligand on the zinc centres to mono-N-methylviologen resulted in the isolation of clean tetra-cationic D4R cubanes 2 and 3. The interaction of these cationic D4R cubane 2 with suitable tetra anionic polyoxometalates of different structural types led us for the first time to isolate [D4R][POM] hybrids 4-6. These thermally stable amorphous hybrid materials, albeit exhibiting moderate surface areas, are found to be mesoporous by N₂ adsorption studies (pore diameters up to 40 nm), were demonstrated to be excellent epoxidation catalysts, exhibiting conversion up to 100%. We are currently designing similar hybrid systems with other types of complex cations and evaluating their properties and catalytic behaviour.

Experimental section

Instruments and methods

The melting points were measured in glass capillaries and are reported uncorrected. IR spectral measurements were carried out using a Bruker Alpha-P Fourier transform spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Ruhr-Universität Bochum. ¹H and ³¹P NMR spectra were recorded using a Bruker Advance DPX-250 spectrometer. The peaks which are not labeled are always solvent peaks and methylbipyridinium protons are labeled as a, b, c and d (see ESI†). Thermogravimetric analysis was carried out with a Perkin Elmer Pyris thermal analysis system, under a stream of nitrogen gas at the heating rate of 10 °C min⁻¹. The film morphologies of the hybrid materials were investigated by using a LEO1530 Gemini Scanning Electron Microscope. Prior to the measurements being recorded, the samples were coated with a thin carbon film.

The starting materials and the products described in this study were found to be stable towards moisture and air, and hence no specific precautions were taken to rigorously exclude air. Commercial grade solvents were purified by employing conventional procedures. The chemicals such as 2,6-di-iso-propylphenol, 4-aminopyridine, 4,4'-bipyridine, ammonium hexa-fluorophosphate (NH₄PF₆), sodium perchlorate (NaClO₄), methyl iodide (MeI), and zinc acetate dihydrate (S.d. Fine Chem.) were used as received. 1-methyl-4,4'-bipyridinium salts and 2,6-di-iso-propylphenyl dihydrogenphosphate (dippH₂) were prepared according to literature reported methods.^{13,14} [Zn(dipp){(CH₃)₂SO}]₄ was also synthesized as white crystals by employing a protocol developed in our laboratory earlier.¹⁵

Synthesis of [Zn(dipp)(4-ampyr]₄·[CH₃OH]₃ (1). To a clear solution of [Zn(dipp){(CH₃)₂SO}]₄ (0.399 g, 0.25 mmol) in methanol (20 mL), a methanolic solution of 4-amino pyridine (0.094 g, 1 mmol) was added. The resulting clear solution was kept on the bench-top for crystallization. After one day, the product crystallizes as colourless crystals. The product was thoroughly washed with cold methanol and dried under vacuum. Yield: 0.31 g (64%). M.p: >275 °C. Anal. Calcd for C71H92N8O20P4Zn4: C, 48.28; H, 6.08; N, 6.26. Found: C, 48.04; H, 5.91; N, 6.31. FT-IR (KBr, cm⁻¹): 3476(br), 3353(br), 3225(br), 2964(vs), 2867(vs), 1639(vs), 1619(w), 1561(w), 1522(vs), 1460(w), 1440(w), 1382(w), 1361(w), 1338(w), 1256(w), 1177(vs), 1063(vs), 1026(vs), 1015(w), 915(vs), 771(vs), 554(s) and 527(vs). ¹H NMR (DMSO-d₆, 400 MHz): δ 7.39 (br, 2H, Ar), 6.90 (m, 3H, Ar-dipp), 6.68 (br, 2H, NH₂), 6.4 (d, 2H, ${}^{3}J_{HH} =$ 6.59 Hz, Ar), 3.6 (septet, 2H, ${}^{3}J_{HH} = 6.9$ Hz, ⁱPr-CH), 0.9 (d, 12H, ${}^{3}J_{HH} = 6.7$ Hz, ${}^{i}Pr-CH_{3}$) ppm. ${}^{31}P$ NMR (DMSO-d₆, 160 MHz): δ –4.5 ppm.

 $[Zn(dipp)(L)]_4[PF_6]_4 \cdot (CH_3OH)_2 \cdot [(CH_3)_2SO]_2$ Synthesis of (2). To a stirred solution of $[Zn(dipp){(CH_3)_2SO}]_4$ (0.16 g, 0.10 mmol) in methanol (20 mL), 1-methyl-4,4'-bipyridinium hexafluorophosphate (0.12 g, 0.40 mmol) in methanol (15 mL) was added. The reaction mixture was stirred for 3 hours while the product precipitated as white solid. The precipitate was thoroughly washed with methanol and dried under vacuum. Yield: 0.14 g (50%). M.p: >275 °C. Anal. Calcd for C₉₈H₁₃₂F₂₄N₈O₂₀P₈S₂Zn₄: C, 42.47; H, 4.80; N, 4.04. Found: C, 41.98; H, 4.71; N, 3.88. FT-IR (neat, cm⁻¹): 2966(br), 1619(s), 1421(w), 1335(w), 1174(vs), 1077(w), 1020(vs), 917(s), 832(vs), 776(s), 750(s), 731(w), 668(w). ¹H NMR (DMSO-d₆, 250 MHz): δ 9.1 (d, 2H, ${}^{3}J_{HH}$ = 6.9 Hz, Ar), 8.8 (d, 2H, ${}^{3}J_{HH}$ = 6.0 Hz, Ar), 8.5 (d, 2H, ${}^{3}J_{HH}$ = 6.7 Hz, Ar), 8.0 (d, 2H, ${}^{3}J_{HH}$ = 6.1 Hz, Ar), 6.9 (m,

3H, Ar-dipp), 4.39 (s, 3H, CH₃-N⁺), 3.6 (septet, 2H, ${}^{3}J_{HH} = 6.9$ Hz, ${}^{i}Pr$ -CH), 1.1 (d, 12H, ${}^{3}J_{HH} = 6.7$ Hz, ${}^{i}Pr$ -CH₃) ppm. ${}^{31}P$ NMR (DMSO-d₆, 100 MHz): $\delta -5.24$ (s, 1P, dipp), -144 (septet, 1P, ${}^{1}J_{PF} = 710$ Hz, PF₆) ppm. ${}^{19}F$ NMR (DMSO-d₆, 250 MHz): $\delta -68.8$, -71.8 ppm.

Synthesis of [**Zn(dipp)(L)**]₄[**C**IO₄]₄·(**C**H₃**OH**)₂ (3). To a solution of [Zn(dipp){(CH₃)₂SO}]₄ (0.041 g, 0.025 mmol) in methanol (20 mL), 1-methyl-4,4'-bipyridinium perchlorate (0.027 g, 0.1 mmol) in methanol (15 mL) was added. The reaction mixture was stirred for overnight while the product precipitated as a white solid. The precipitate was filtered, thoroughly washed with methanol and dried under vacuum. Yield: 0.016 g (26%). M.p: >275 °C. Anal. Calcd for C₉₄H₁₂₀Cl₄N₈O₃₄P₄Zn₄: C, 46.40; H, 4.97; N, 4.60. Found: C, 46.25; H, 4.69; N, 4.50. ¹H NMR (DMSO-d₆, 250 MHz): δ 9.1 (d, 2H, ³J_{HH} = 6.7 Hz, Ar-d), 8.8 (d, 2H, ³J_{HH} = 6.0 Hz, Ar-a), 8.6 (d, 2H, ³J_{HH} = 6.7 Hz, Ar-c), 8.0 (d, 2H, ³J_{HH} = 6.3 Hz, Ar-b), 7.0 (m, 3H, Ar-dipp), 4.38 (s, 3H, CH₃-N⁺), 3.6 (septet, 2H, ³J_{HH} = 6.9 Hz, ⁱPr-CH), and 1.1 (d, 12H, ³J_{HH} = 6.7 Hz, ⁱPr-CH₃) ppm. ³¹P NMR (DMSO-d₆, 100 MHz): δ –5.2 ppm.

Synthesis of [Zn (dipp)(L)]₄·[Mo₈O₂₆] (4). To a solution of $[Zn(dipp)(L)]_4[PF_6]_4$ (0.53 g, 0.21 mmol) in acetonitrile (15 mL), a solution of [(TBA)₄(Mo₈O₂₆)] (0.43 g, 0.20 mmol) in acetonitrile (15 mL) was added. The reaction mixture was stirred for four hours while the desired product precipitated as a white solid. The precipitate was filtered and thoroughly washed with methanol (30 mL) and acetonitrile (30 mL). The compound was dried under vacuum. Yield: 0.50 g (60%). M.p: >275 °C. Anal. Calcd for C₉₂H₁₁₂Mo₈N₈O₄₂P₄Zn₄: C, 35.02; H, 3.58; N, 3.55. Found: C, 34.66; H, 3.93; N, 3.46. FT-IR (neat, cm⁻¹): 2962(br), 1619(s), 1422(w), 1332(w), 1256(w), 1174(vs), 1079(w), 1046(w), 1019(vs), 912(vs), 843(s), 811(s), 779(vs), 714(s), 665(s). ¹H NMR (DMSO-d₆, 250 MHz): δ 9.2 (d, 2H, ³J_{HH} = 6.6 Hz, Ar-d), 8.9 (d, 2H, ${}^{3}J_{HH}$ = 6.1 Hz, Ar-a), 8.7 (d, 2H, ${}^{3}J_{HH}$ = 6.6 Hz, Ar-c), 8.1 (d, 2H, ³J_{HH} = 6.1 Hz, Ar-b), 7.1 (m, 3H, Ar-dipp), 4.4 (s, 3H, CH_3-N^+), 3.7 (septet, 2H, ${}^{3}J_{HH} = 6.7$ Hz, ${}^{i}Pr-CH$), and 1.2 (d, 12H, ${}^{3}J_{HH} = 6.9$ Hz, ${}^{1}Pr-CH_{3}$) ppm. ${}^{31}P$ NMR (DMSO-d₆, 100 MHz): δ –5.2 ppm.

Synthesis of [Zn(dipp)(L)]₄·[PMo₁₁VO₄₀] 12H₂O (5). To a solution of [Zn(dipp)(L)]₄[PF₆]₄ (0.07 g, 0.02 mmol) in acetonitrile (5 mL), a solution of $[(TBA)_4(PMO_{11}VO_{40})]$ (0.06 g, 0.02 mmol) in acetonitrile (5 mL) was added. The reaction mixture was stirred for four hours while the product precipitated as a yellowish solid. The precipitate was filtered and thoroughly washed with acetonitrile (40 mL) and dried under vacuum. Yield: 0.08 g (77%). M.p: >275 °C. Anal. Calcd for C₉₂H₁₃₆Mo₁₁N₈O₆₈P₅VZn₄: C, 29.48; H, 3.01; N, 2.99. Found: C, 27.87; H, 3.46; N, 2.83. FT-IR (neat, cm⁻¹): 2992(br), 1620(s), 1464(w), 1330(w), 1176(br), 1074(s), 1055(s), 1019(vs), 945(vs), 872(s), 789(vs). ¹H NMR (DMSO-d₆, 250 MHz): δ 9.1 (d, 2H, ${}^{3}J_{HH}$ = 7.1 Hz, Ar-d), 8.8 (d, 2H, ${}^{3}J_{HH}$ = 6.0 Hz, Ar-a), 8.6 (d, 2H, ${}^{3}J_{HH}$ = 6.9 Hz, Ar-c), 8.0 (d, 2H, ${}^{3}J_{HH}$ = 6.1 Hz, Ar-b), 7.0 (m, 3H, Ar-dipp), 4.4 (s, 3H, CH_3-N^+), 3.7 (septet, 2H, ${}^{3}J_{HH} = 6.7$ Hz, ⁱPr-CH), and 1.1 (d, 12H, ${}^{3}J_{HH}$ = 6.9 Hz, ⁱPr-CH₃) ppm. 31 P NMR (DMSO-d₆, 100 MHz): δ -4.5 (POM), -5.2 (zinc cubane) ppm.

Synthesis of [Zn(dipp)(L)]₄·[SiMo₁₂O₄₀] (6). To a solution of $[Zn(dipp)(L)]_4[PF_6]_4$ (0.05 g, 0.02 mmol) in acetonitrile (5 mL), a solution of $[TBA]_4[(SiMO_{12}O_{40})]$ (0.054 g, 0.02 mmol) in acetonitrile (5 mL) was added. The reaction mixture was stirred for four hours while the desired product precipitated as greenish solid. The precipitate was filtered and thoroughly washed with acetonitrile (40 mL) and dried under vacuum. Yield: 0.07 g (76%). M.p: >275 °C. Anal. Calcd for C₉₂H₁₁₂Mo₁₂N₈O₅₆P₄-SiZn₄: C, 29.15; H, 2.98; N, 2.96. Found: C, 27.93; H, 2.75; N, 2.87. FT-IR (neat, cm⁻¹): 2963(br), 1622(s), 1467(w), 1332(w), 1177(s), 1012(s), 944(s), 899(vs), 785(vs). ¹H NMR (DMSO-d₆, 250 MHz): δ 9.2 (d, 2H, ${}^{3}J_{HH}$ = 6.9 Hz, Ar-d), 8.9 (d, 2H, ${}^{3}J_{HH}$ = 6.1 Hz, Ar-a), 8.7 (d, 2H, ${}^{3}J_{HH}$ = 6.9 Hz, Ar-c), 8.1 (d, 2H, ${}^{3}J_{HH}$ = 6.1 Hz, Ar-b), 7.1 (m, 3H, Ar-dipp), 4.4 (s, 3H, CH₃-N⁺), 3.7 (septet, 2H, ${}^{3}J_{HH} = 6.7$ Hz, i Pr-CH), 1.2 (d, 12H, ${}^{3}J_{HH} = 6.9$ Hz, ⁱPr-CH₃) ppm. ³¹P NMR (DMSO-d₆, 100 MHz): δ –5.2 ppm.

Single crystal X-ray diffraction studies

The X-ray diffraction intensities for compound **1** were collected on Oxford Xcalibur 2 diffractometer with a Sapphire2 CCD detector. All the calculations pertaining to structure solutions and refinement were carried out using the programs included in the WinGX module.¹⁶ The structure solution was achieved by direct methods using SIR-92.¹⁷ The final refinement of the structure was carried out using full least-squares methods on F^2 using SHELXL-97.¹⁸

N₂ sorption measurements

Gas adsorption measurements were performed using a Quantachrome Autosorb 1-C analyzer. UHP-grade gases were used in measurements without further purification. The N₂ adsorption measurements were performed at 77 K. Prior to gas adsorption measurements, the samples were activated at room temperature for 24 h and at 100 °C for 48 h under ultrahigh vacuum (10^{-8} mbar).

General procedure for the catalytic oxidation by phosphatepolyoxometalate hybrids

A two-necked round bottom flask connected with a condenser and Schlenk adaptor was charged with substrate (0.2 mmol) and hydrogen peroxide (30%, 5 mL). Catalyst (hybrid polyoxometalate, 0.35 mmol) was added to the above solution under N_2 atmosphere. Reaction mixture was then heated at 85–90 °C at constant stirring. Reaction was monitored by GC or GCMS by collecting sample and analyzing at regular intervals.

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Notes and references

- (a) I. V. Kozhevnikov, *Catalysis by Polyoxometalates*, Wiley, Chichester, England, 2002; (b) C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, 143, 407; (c) T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, 1996, 41, 113; (d) R. Neumann, *Prog. Inorg. Chem.*, 1998, 47, 317.
- 2 (a) R. Neumann and A. M. Khenkin, *Chem. Commun.*, 1998, 1967; (b) R. Ben-Daniel, L. Weiner and R. Neumann, *J. Am. Chem. Soc.*, 2002, 124, 8788; (c) R. Ben-Daniel and R. Neumann, *Angew. Chem., Int. Ed.*, 2003, 42, 96; (d) A. M. Khenki and R. Neumann, *J. Am. Chem. Soc.*, 2002, 124, 4198; (e) A. M. Khenkin and R. Neumann, *J. Org. Chem.*, 2002, 67, 7075.
- 3 (a) C. L. Hill, Chem. Rev., 1998, 98, 1; (b) Z. Karimi and A. R. Mahjoub, Catal. Commun., 2011, 12, 984; (c) W. Q. Kan, J. Yang, Y. Y. Liu and J. F. Ma, Inorg. Chem., 2012, 51, 11266; (d) H. Wu, J. Yang, Z. M. Su, S. R. Batten and J. F. Ma, J. Am. Chem. Soc., 2011, 133, 11406; (e) A. Dolbecq, E. Dumas, C. R. Mayer and P. Mialane, Chem. Rev., 2010, 110, 6009; (f) P. Gouzerh and A. Proust, Chem. Rev., 1998, 98, 77.
- 4 (a) I. Bar-Nahum, A. M. Khenki and R. Neumann, J. Am. Chem. Soc., 2004, 126, 10236; (b) D. Hagrman, C. Zubieta, D. J. Rose, J. Zubieta and R. C. Haushalter, Angew. Chem., Int. Ed., 1997, 36, 873; (c) Y. Xu, J. Q. Xu, K. L. Zhang, Y. Zhang and X. Z. You, Chem. Commun., 2000, 153; (d) J. Q. Sha, L. Y. Liang, J. W. Sun, A. X. Tian, P. F. Yan, G. M. Li and C. W. Wang, Cryst. Growth Des., 2012, 12, 894; (e) Y. F. Li, D. G. Hubble, R. G. Miller, H. Y. Zhao, W. P. Pan, S. Parkin and B. Yan, Polyhedron, 2010, 29, 3324; (f) J. Wang, P. Ma, Y. Shen and J. Niu, Cryst. Growth Des., 2008, 8, 3130.
- 5 (a) C. L. Hill and R. B. Brown, J. Am. Chem. Soc., 1986, 108, 536; (b) D. Mansuy, J. F. Bartoli, P. Battioni, D. K. Lyon and R. G. Finke, J. Am. Chem. Soc., 1991, 113, 7222; (c) H. Weiner, Y. Hayashi and R. G. Finke, Inorg. Chem., 1999, 38, 2579; (d) X. Zhang, K. Sasaki and C. L. Hill, J. Am. Chem. Soc., 1996, 118, 4809; (e) R. Neumann and C. Abu-Gnim, J. Chem. Soc., Chem. Commun., 1989, 13245; (f) R. Neumann and C. Abu-Gnim, J. Am. Chem. Soc., 1990, 112, 6025; (g) E. Steckhan and C. Kandzia, Synlett, 1992, 139; (h) R. Neumann and A. M. Khenkin, Chem. Commun., 1998, 1967; (i) R. Ben-Daniel, L. Weiner and R. Neumann, J. Am. Chem. Soc., 2002, 124, 8788; (j) R. Ben-Daniel and R. Neumann, Angew. Chem., Int. Ed., 2003, 42, 96; (k) A. M. Khenkin and R. Neumann, J. Am. Chem. Soc., 2002, 124, 4198; (l) A. M. Khenkin and R. Neumann, J. Org. Chem., 2002, 67, 7075; (m) R. Neumann and M. Dahan, Nature, 1997, 388, 353; (n) R. Neumann and M. J. Dahan, J. Am. Chem. Soc., 1998, 120, 969; (o) H. Weiner and R. G. Finke, J. Am. Chem. Soc., 1999, 121, 9831; (p) Y. Nishiyama, Y. Nakagawa and N. Mizuno, Angew. Chem., Int. Ed., 2001, 40, 3639.
- 6 (a) M. V. Vasylyev and R. Neumann, J. Am. Chem. Soc., 2004, **126**, 884; (b) V. Mirkhani, M. Moghadam,

- S. Tangestaninejad, I. Mohammadpoor-Baltork and N. Rasouli, *Inorg. Chem. Commun.*, 2007, **10**, 1537; (c) V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, E. Shams and N. Rasouli, *Appl. Catal., A*, 2008, **334**, 106; (d) V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork and N. Rasouli, *Catal. Commun.*, 2008, **9**, 219; (e) V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork and N. Rasouli, *Catal. Commun.*, 2008, **9**, 2171.
- 7 R. Murugavel, S. Kuppuswamy, R. Boomishankar and A. Steiner, *Angew. Chem., Int. Ed.*, 2006, **45**, 5536.
- 8 (a) R. Murugavel, S. Kuppuswamy, N. Gogoi, R. Boomishankar and A. Steiner, *Chem.-Eur. J.*, 2010, 16, 994; (b) R. Murugavel, S. Kuppuswamy, N. Gogoi and A. Steiner, *Inorg. Chem.*, 2010, 49, 2153.
- 9 (a) L. Michaelis and E. S. Hill, J. Gen. Physiol., 1933, 16, 859; (b) N. Mercier, Eur. J. Inorg. Chem., 2013, 19; (c) C. D. Clark, J. D. Debad, E. H. Yonemoto, T. E. Mallouk and A. J. Bard, J. Am. Chem. Soc., 1997, 119, 10525; (d) E. L. Clennan, Coord. Chem. Rev., 2004, 248, 477.

- 10 R. Murugavel, M. Sathiyendiran and M. G. Walawalkar, Inorg. Chem., 2001, 40, 427.
- 11 P. Schneider, Appl. Catal., A, 1995, 129, 157.
- 12 (a) N. Mizuno, C. Nozaki, I. Kiyoto and M. Misono, J. Catal., 1999, 182, 285; (b) N. Mizuno, C. Nozaki, I. Kiyoto and M. Misono, J. Am. Chem. Soc., 1998, 120, 9267; (c) X. Zhang, Q. Chen, D. C. Duncan, R. J. Lachicotte and C. L. Hill, Inorg. Chem., 1997, 36, 4381; (d) N. S. Antonova, J. J. Carbó, U. Kortz, O. A. Kholdeeva and J. M. Poblet, J. Am. Chem. Soc., 2010, 132, 7488.
- 13 G. M. Kosolapoff, C. K. Arpke, R. W. Lamb and H. Reich, *J. Chem. Soc. C*, 1968, 7, 815.
- 14 D. J. Feng, X. Q. Li, X. Z. Wang, X. K. Jiang and Z. T. Li, *Tetrahedron*, 2004, **60**, 6137.
- 15 S. Kuppuswamy, PhD thesis, IIT Bombay, 2008.
- 16 L. J. Farrugia, WinGX, Version 1.64.05, J. Appl. Crystallogr, 1999, 32, 837.
- 17 A. Altomare, G. Cascarano, C. Giacovazzo and A. Gualardi, J. Appl. Crystallogr., 1993, 26, 343.
- 18 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.