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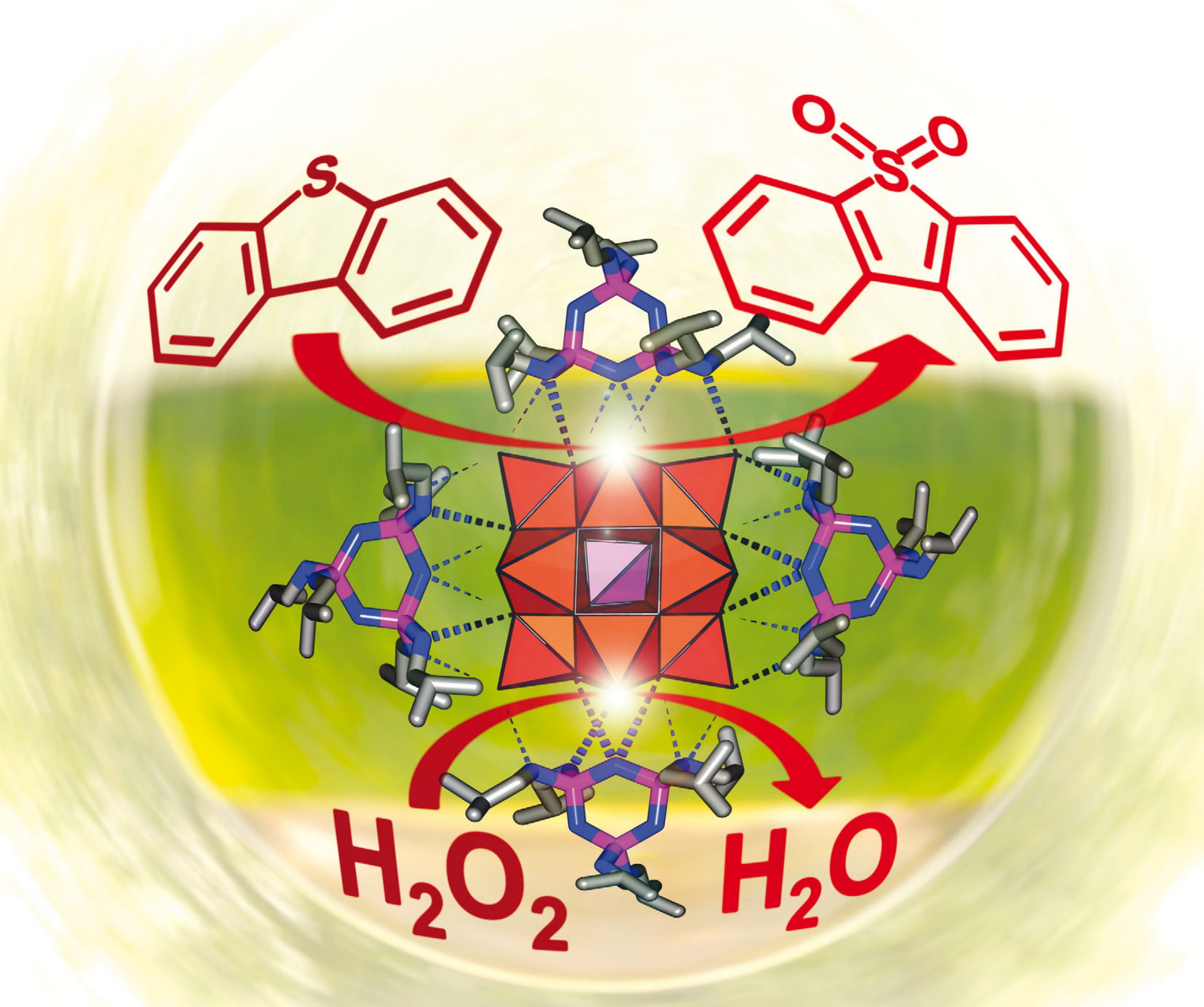

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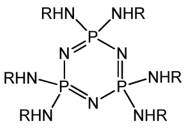
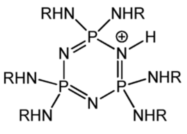
Polyoxometalate–phosphazene salt aggregates comprising cyclophosphazene cations are highly efficient catalysts for environmentally benign biphasic oxidations with hydrogen peroxide. These catalysts self-assemble *in situ* simply by mixing commercial Keggin POMs and readily available phosphazenes.

Nanosized metal–oxygen cluster anions – polyoxometalates (POMs) – form a class of compounds unique in its structural variety and functional versatility.[1] These compounds, which consist of O-sharing MO_x polyhedra (most often M = Mo^{VI}, W^{VI} and V^{V}), have found applications in various disciplines,[2] of which catalysis is by far the most important. This includes large-scale industrial processes such as the oxidation of methacrolein to methacrylic acid, the hydration of alkenes to alcohols and the synthesis of ethyl acetate by direct addition of acetic acid to ethene.[2e]

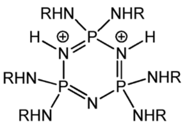
In the search for highly active catalysts for environmentally benign biphasic oxidations with hydrogen peroxide we have investigated aggregates comprising Keggin type polyanions $[XM_{12}O_{40}]^{m-}$ {X = P^{V} (m = 3) and Si^{IV} (m = 4)} and lipophilic cyclophosphazene cations $[(RNH)_6P_3N_3H_n]^{n+}$ (n = 1 or 2). Cyclic and polymeric phosphazenes are renowned for their chemical and thermal robustness. They have been used as high performance elastomers, fire retardants, polymeric electrolytes and also for biomedical applications.[3] Cyclophospazenes with amino substituents {$(RNH)_6P_3N_3$, labelled from here **RPN**} are strong bases; one or two ring N-centres are protonated in the presence of Brønsted acids yielding mono and dications, **RPN**H^+ and **RPN**H_2^{2+}, respectively.[4] These compounds are easy to prepare on a large scale in one-step reactions from commercially available hexachloro cyclotriphosphazene and a wide range of primary amines.[5] Their phosphazene backbone is remarkably inert even towards concentrated acids and bases at elevated temperatures.[6] These compounds are highly soluble in non-polar solvents, but at the same time provide multiple hydrogen bonding sites, which makes them versatile building blocks for supramolecular assemblies.[7] To our knowledge, cyclophosphazenes have not been applied as surfactants in catalysis. $[(Me_2N)_6P_3N_3H]_2[Mo_6O_{19}]$ is the only previously reported POM–cyclophosphazene aggregate.[8] However, this complex contains a relatively small dianion and lacks the array of multiple hydrogen bonding sites.



RPN



RPNH^+



RPNH_2^{2+}

Aggregates of **RPN** {R = isopropyl (iPr), isobutyl (iBu) and benzyl (Bz)} and Keggin heteropoly acids $H_4SiW_{12}O_{40}$ (H_4SiW), $H_3PW_{12}O_{40}$ (H_3PW) and $H_3PMo_{12}O_{40}$ (H_3PMo) form readily upon mixing the two components in methanol. The heteropoly acids were used as crystalline hydrates roughly containing 20 H_2O per Keggin unit. They were combined with the phosphazenes in POM/**RPN** molar ratios of 1 : 4 for H_4SiW and 1 : 3 and 1 : 6 for H_3PMo and H_3PW. The salt aggregates crystallized from methanol upon slow evaporation of the solvent. Crystals suitable for X-ray structure determination were obtained from batches [H_4SiW/iBuPN (1 : 4)], [H_3PW/iPrPN (1 : 3)], [H_3PW/iBuPN (1 : 3)] and [H_3PW/iPrPN (1 : 6)].

The crystals obtained from [H_4SiW/iBuPN (1 : 4)] yielded a structure of composition $[iBuPNH]_4[SiW]\cdot 2CH_3OH$. Although H-atoms could not be located from difference maps, the bond length alternation within the P_3N_3 ring is a reliable indicator that protonation at ring N sites has occurred. While the ring bonds of neutral **RPN** are in the region of 1.60 Å,[5] cations **RPN**H^+ show substantial elongation of bonds around the protonated ring N site and shortening of bonds around the non-protonated sites.[9] This pattern is also observed in $[iBuPNH]_4[SiW]$. Furthermore, the ring N atom connected *via* the long ring bonds (averaging 1.66 Å) is also in hydrogen bonding distance to the polyanion. Fig. 1a shows how four $[iBuPNH]^+$ ions surround one $[SiW]^{4-}$ ion. Remarkably, this assembly features twenty NH···O interactions to which every phosphazene ligand contributes one ring NH and four exocyclic

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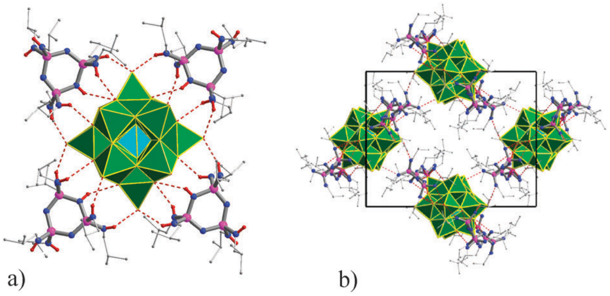


Fig. 1 Crystal structure of $[iBuPNH]_4[SiW]\cdot 2CH_3OH$: (a) $[iBuPNH]_4[SiW]$ unit, (b) crystal packing. WO_x polyhedra, green; SiO_4, turquoise; P, purple; N, blue; H, red; alkyl groups, grey; hydrogen bonds are drawn as dotted lines.

NH sites. Further NH···O contacts involving the two remaining exocyclic NH sites result in a 3D networked structure (Fig. 1b).

It is interesting to note that 1 : 3 mixtures of triprotic H_3PW, which is a stronger Brønsted acid than H_4SiW,[2e] and **RPN** yielded crystals which contained only two phosphazene ions for every polyoxometalate ion. However, close examination of the crystal structures revealed that the phosphazenes exist as mono- and dications, $[\mathbf{RPN}H]^+$ and $[\mathbf{RPN}H_2]^{2+}$, respectively, while the polyoxometalate ion carries the expected −3 charge. The crystals exhibit compositions $[iPrPNH][iPrPNH_2][PW]\cdot 6CH_3OH$ and $[iBuPNH][iBuPNH_2][PW]\cdot 3H_2O\cdot CH_3OH$. In both cases the extra proton is disordered between two symmetrically equivalent cations across a hydrogen bonded chain of solvent molecules. Fig. 2 illustrates the disorder of $[iPrPNH][iPrPNH_2][PW]\cdot 6CH_3OH$ where the two phosphazene rings are connected *via* H-bonds across two methanol molecules (Fig. 2a). This is also indicated by alternations in the bond lengths of the P_3N_3 rings, which vary between long (around the fully protonated site N1), short (around the non-protonated site N3) and medium (around the partially protonated site N2, which binds the disordered proton).

Crystals were also obtained from 1 : 6 mixtures of H_3PW and iBuPN. However, their poor quality only permitted the location of W and P atoms, which confirmed that the 1 : 6 ratio is retained in the crystal structure. The six phosphazene ligands surround the polyoxometalate ion in an octahedral fashion (Fig. 2b, see also ESI†). Considering the presence of $[PW]^{3-}$ ions the most likely composition of these crystals is $[iBuPNH]_3[PW]\cdot 3iBuPN\cdot x$ solvent containing both cationic and neutral phosphazene ligands.

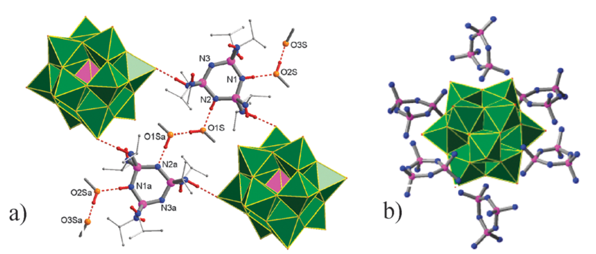


Fig. 2 (a) Crystal structure of $[iPrPNH][iPrPNH_2][PW]\cdot 6CH_3OH$ highlighting the disorder of the proton (see Fig. 1 for colour coding, O1S and O1Sa are part of methanol molecules). Note that there is a centre of inversion; therefore the two phosphazenes are symmetrically equivalent. As a result, the proton is bonded to either N2 or N2a. Changing between the two states involves shifting H-atoms along the H-bonding chain N2···O1S···O1Sa···N2a. Methanol H-atoms were not considered in the refinement, but were added here to illustrate the connectivity of the H-bonding chain. (b) Octahedral assembly of $[iBuPN]_3[iBuPNH]_3[PW]$ modelled at the positions of W and P atoms.

The crystal structures of the POM–**RPN** aggregates show that the phosphazene ligands are able to encapsulate the large polyanions effectively *via* multiple H-bonding interactions. They reveal polyprotic ligand behaviour that utilizes not only the monocationic ligand $[\mathbf{RPN}H]^+$ but also the neutral and dicationic systems. Furthermore, the POM–phosphazene aggregates exhibit high thermal stability. Thermogravimetric analyses show decomposition onsets ranging from 260 (PW-iPr) to 340 °C (SiW-iBu). The UV-Vis and FTIR spectra of the aggregates correspond well to the spectra of POM acid hydrates $H_m[XM_{12}O_{40}]\cdot xH_2O$, which indicates that the presence of the highly redox-stable phosphazenes has little effect on the electronic structure of the POM clusters (see ESI† for details).

Catalytic studies showed that POM–phosphazene aggregates serve as highly efficient catalysts for biphasic oxidations with hydrogen peroxide. We looked at two reactions of significant practical importance – oxidative desulfurization[10] and olefin epoxidation.[11] Both are catalyzed by POMs in homogeneous or two-phase systems and are the subject of much current interest. There is compelling evidence that Keggin polyanions are transformed by excess H_2O_2 in solution to form peroxo polyoxometalate species, *e.g.* $\{PO_4[WO(O_2)_2]_4\}^{3-}$. These have been suggested to be the active intermediates in oxidations with H_2O_2.[11] Tungsten POMs are usually more active than the corresponding molybdenum derivatives. Biphasic oxidation in a water–organic system is particularly attractive, as it can facilitate product separation. But it requires an efficient phase-transfer agent to effectively move the peroxo polyanions into the organic phase. Commonly, POM aggregates containing quaternary ammonium cations with C_8–C_{18} alkyl groups are used; these, however, are often cumbersome to prepare. We therefore anticipated that the POM–phosphazene aggregates would function as effective and easily applicable peroxide carriers between the phases.

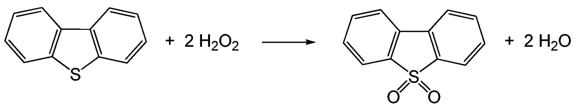
Oxidative desulfurization catalyzed by tungsten POMs using 30% H_2O_2 as a "green" oxidant has been developed as a promising method for deep desulfurization of transportation fuel.[10c] The oxidation of dibenzothiophene (DBT) (eqn (1)) is typically employed as a model reaction for catalyst testing. We found that POM–**RPN** aggregates are highly active catalysts for DBT oxidation with H_2O_2 in a biphasic system, *e.g.* toluene–water (Table 1), yielding DBT sulfone as the sole product. The POM–**RPN** aggregates can be introduced in the reaction system as pre-synthesized compounds or, if preferred, POM and **RPN** components can simply be added separately to form the active catalyst *in situ.* Catalyst activity was found to increase with the size of the R group in line with increasing phase-transfer efficiency of **RPN**: iPr < iBu < Bz (entries 1–3). The activity also increased with the [BzPN]/[POM] molar ratio, levelling off at a ratio of 6 : 1 (entries 4–6). Unexpectedly, PMo exhibited a higher activity than PW (entries 5 and 7), whereas SiW showed no activity at all. The latter is in agreement with the well-known stability of SiW to degradation in solution[2e] and its resistance to form peroxo species. It is important to note that practically no decomposition of H_2O_2 to molecular oxygen took place in this system, giving >99% efficiency for H_2O_2 utilization. The oxidation of DBT in the presence

Table 1 Oxidation of DBT by H_2O_2 in toluene–H_2O two-phase system in the presence of POM–phosphazene catalysts[a]

Entry	POM	**RPN**	Temp. [°C]	Conversion [%]	H_2O_2 efficiency [%]
1	PW[b]	iPrPN	40	38	99
2	PW[b]	iBuPN	40	89	99
3	PW[b]	BzPN	40	94	99
4	PW[c]	BzPN	60	81	99
5	PW	BzPN	60	98	99
6	PW[d]	BzPN	60	100	99
7	PMo	BzPN	60	100	99

[a] Toluene (10 mL), DBT (0.50 mmol, 1 wt%), aqueous 30% H_2O_2; molar ratios: [DBT]/[POM] = 90 : 1, [DBT]/[H_2O_2] = 1 : 3, [**RPN**]/[POM] = 4 : 1; 30 min time. DBT sulfone was the only reaction product. [b] [H_2O_2]/[POM] = 20 : 1. [c] [BzPN]/[POM] = 2 : 1. [d] [BzPN]/[POM] = 6 : 1.

of PW–BzPN was found to be first order in DBT (Fig. S7, ESI†). The phosphazene was stable under the reaction conditions, which was confirmed by monitoring the reactions with ^{31}P NMR. In the presence of PW–BzPN (1 : 6) and PMo–BzPN (1 : 4) the oxidation of DBT proceeded with 100% conversion at 60 °C (Table 1). Moreover, the catalyst could be recovered and reused without loss of activity (see ESI†). This compares well with the best results reported so far. Jiang *et al.*[10b] used amphiphilic decatungstate $[(CH_3)_3NC_{16}H_{33}]_4W_{10}O_{32}$ as the catalyst under similar conditions and observed similar DBT conversions (99.6%), but without giving the H_2O_2 efficiency. Similar results have also been reported for the $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst.[10c] These catalysts, however, have to be pre-synthesized *via* a cumbersome procedure,[10b] which is not required for the POM–**RPN** system. The other advantage of our system is that molybdenum based systems can be used instead of tungsten, which reduces the catalyst weight by 25–30%.



(1)

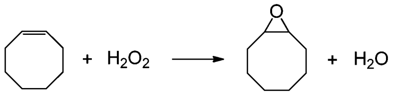
We have also examined the epoxidation of cyclooctene (eqn (2)), the standard screening test for epoxidation catalysts (Table 2). The reaction was carried out in a biphasic toluene–water system at 25–50 °C using 10% H_2O_2 as the oxidant and a mixture of PW and BzPN (1 : 4–1 : 6) as the catalyst. This catalyst was very efficient even at room temperature, yielding >99% epoxycyclooctane with >99% efficiency of H_2O_2 utilization in 3 h reaction time. Again, the decomposition of H_2O_2 was negligible, and the catalyst could be recovered and reused. Our catalyst can be compared favourably with one of the best POM epoxidation catalysts – the lacunary silicotungstate $(nBu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ reported by Kamata *et al.*[11c] This catalyst epoxidizes cyclooctene with 30% H_2O_2 in homogeneous MeCN solution at 32 °C and otherwise under similar conditions, giving also 99% epoxide yield with >99% H_2O_2 efficiency. But in contrast to the straightforward preparation of PW–BzPN, the synthesis of lacunary silicotungstate is an elaborate procedure.

Table 2 Biphasic epoxidation of cyclooctene by 10% H_2O_2 catalyzed by PW–BzPN[a]

Temperature [°C]	[BzPN]/[PW] [mol/mol]	Time [h]	Conversion [%]	Yield[b] [%]
25	6	3.0	>99	>99
50	6	0.5	>99	>99
50	4	1.5	>99	>99

[a] Toluene (10 mL), cyclooctene (7.0 mmol, 1.0 mL), aqueous 10% H_2O_2 (1 mmol, 0.3 mL), $H_3PW_{12}O_{40}\cdot 20H_2O$ (5.53 μmol, 0.018 g). [b] Yield based on the initial amount of H_2O_2.

Besides, our reaction system is safer since it only requires dilute 10% rather than 30% H_2O_2.



(2)

In conclusion, we have synthesized and structurally characterised novel POM–phosphazene salt aggregates and demonstrated their high efficiency as amphiphilic catalysts for environmentally benign oxidations with H_2O_2 in biphasic systems. These catalysts self-assemble *in situ* simply by mixing commercial Keggin POMs and readily available phosphazenes. The phosphazene ligands provide large arrays of hydrogen bonding sites enabling the effective encapsulation of polyanions. Further studies directed to analogous reactions and their mechanistic understanding are underway.

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