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Shining a light on the photo-sensitisation of organic-inorganic hybrid polyoxometalates

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Finding new ways of using visible light (or, more specifically, solar irradiation) to drive commercially significant and/or challenging chemical processes is an ongoing research goal. Polyoxometalates (POMs) are discrete, metal-oxide clusters which are cheap, robust and easily synthesized but can also act as versatile molecular building blocks, allowing for astonishing variety in their structures and properties. In particular, the rich redox chemistry and inherent photo-activity of POMs makes them attractive for use in a variety of photochemical applications however POMs characteristically only absorb strongly in the UV region. In this perspective, we discuss the various strategies which have been employed in order to sensitize POMs to visible light, with a particular focus on hybrid inorganic-organic POM species. We will discuss the two clear photo-activation mechanisms which have been developed to date and provide an outlook on some of the possible future directions of the field.

1. Introduction

An increasing worldwide population places significant and ever-growing pressures on the generation of energy, manufacturing of essential feedstock chemicals and the supply of clean water.[1] As such, research efforts into the development of new materials for the generation solar fuels, water-remediation and more efficient catalytic processes towards energy and feedstock usage continue to be a key goal in the chemical sciences.[2] Polyoxometalates (POMs) are a class of materials that show great promise towards overcoming these challenges. This diverse class of polyanionic metal oxide clusters, first reported by Berzelius in 1824,[3] can be considered as discrete molecular analogues of traditional solid-state metal oxides and exhibit rich redox, catalytic and photocatalytic properties.[4-6] As a result, POMs have already found application in several industrial catalytic processes, such as the conversion of isobutane to methacrylic acid,[7-9] and the deep desulfurisation of crude hydrocarbons.[10, 11]

Typically, POMs are formed from group 5 and 6 metal oxoanions, in particular those of tungsten, molybdenum or vanadium in their highest oxidation states.[12] In solution, the individual oxometalate precursors undergo condensation-driven self-assembly, typically – though not exclusively – in the presence of templating anions such as SiO_4^{4-} or PO_4^{3-}, to form oligomeric metal oxide clusters (Figure 1).[13] Careful control of the reaction parameters, such as temperature, pH, ionic strength, or by the introduction of particular counter cations or redox species, can give rise to an astonishing range of new molecular architectures and topologies.[5, 13]
The chemistry of the tungstate- and molybdate-based species is dominated by the formation of stable cluster species with the general formula $[X_aM_bO_c]^{n-}$ (M = W, Mo), where the additional heteroelement, X, of the templating anion(s) are directly incorporated into the cluster core. The most common structures of these so-called heteropolyoxometalates are the $[XM_6O_{24}]^{n-}$ Evans-Anderson, $[XM_{12}O_{40}]^{n-}$ Keggin and $[X_2M_{18}O_{62}]^{n-}$ Wells-Dawson structures (see Figure 2). In the absence of templating anions, isopolyoxometalates are formed, of which the most commonly studied are the Lindqvist structure $[M_6O_{19}]^{n-}$, and the decatungstate anion $[W_{10}O_{32}]^{4-}$. The latter in particular has received considerable attention due to its UV-driven photocatalytic properties. In contrast, the chemistry of polyoxovanadates is typified by small to medium- sized clusters typically consisting of between 4 and 30 vanadium ions, the

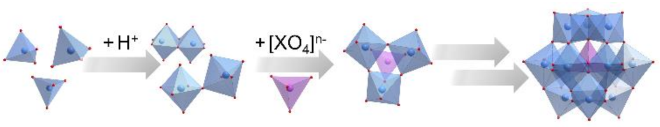

Figure 1. A simplified schematic of the typical polyoxometalate self-assembly process. Acid mediated condensation of tetrahedral [MO4]n- oxoanions (left) leads to the formation of corner- and/or edge-linked dimeric or trimeric units. Further condensation of these species, either in the presence or absence of an additional heteroatomic templating species, e.g. [XO4]n- (X = P, S, Si, etc.), leads to further formation of intermediate secondary building units and, finally, formation of the isolable polyoxometalate product (right). Colour code: {MOx} = blue polyhedra; {XO4} = purple polyhedra; O = red. Cations are omitted for clarity.

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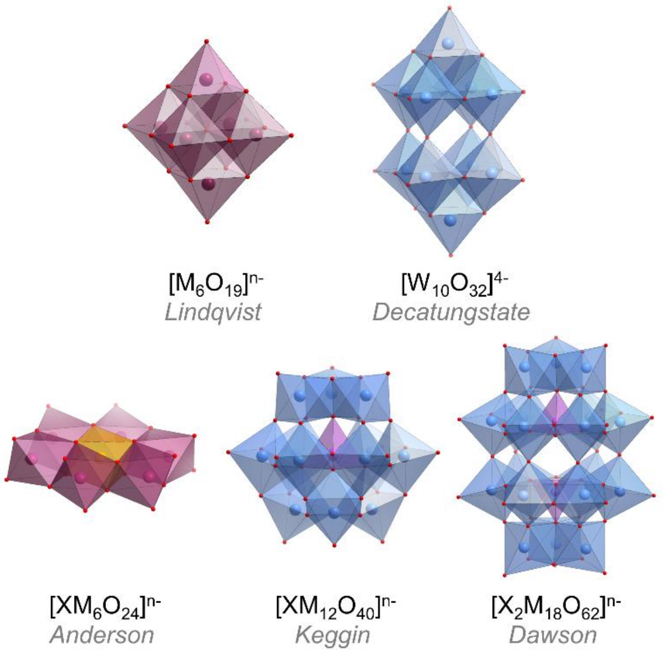


Figure 2. Structures of some archetypical POM clusters. Top: Lindqvist and Decatungstate isopolyoxoanions and, bottom: Anderson, Keggin and Dawson heteropolyoxoanions. Colour code: {MoO_6} = plum polyhedra; {WO_6} = blue polyhedra; {XO_6} = orange polyhedra; {XO_4} = purple polyhedra; O = red. Cations are omitted for clarity.

topology of which is often controlled by electrostatic templating with a variety of small anionic or neutral guests.[14]

1.2. Functionalization Approaches in Polyoxometalate Chemistry

One of the most interesting facets of POM chemistry and a key driving force in the rapid growth of the field over the past few decades is their vast structural and compositional diversity. In large part, this arises from the ease with which POM clusters can be controllably functionalized, either *via* purely inorganic routes (e.g. to yield new, functional heterometallic species) or by hybridization of the inorganic POM cluster with complimentary organic, or organometallic, components: thus forming so-called organic-inorganic *hybrid-POM* complexes. Generally speaking, there are three key functionalization approaches which are commonly adopted: (i) substitution of addenda atoms in the POM cluster with either main-group or transition metal atoms; (ii) counter cation exchange (i.e. replacing protons or group 1 metal cations with organocations, for example), or; (iii) substitution of addenda atoms with organic moieties. To date, these methods have been widely and successfully employed as a route to access new extended materials comprised of individual POM building units, or as a method to introduce enhanced catalytic, photocatalytic, magnetic and/or electrochemical properties.[14-19] Whilst a full accounting of these approaches is beyond the scope of this *Perspective*, a brief outline of each is given in the following:

i) Inorganic Modification: The functionalization of POMs to yield purely inorganic cluster species typically follows one of two routes: either *via* one-pot synthesis of the POM cluster in the presence of a suitable transition metal or main-group cations, or; by the controlled addition of said cations to one or more vacant sites on the POM. These reactive vacancies are generated by controlled partial hydrolysis of the parent POM anion to remove one or more addenda atoms, where the resultant species are commonly termed *lacunary* POMs and can be employed as polydentate ligands towards a huge variety of secondary heteroatoms.[20]

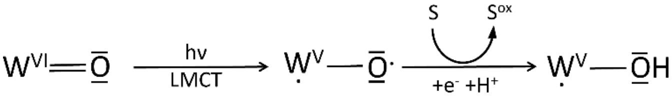
Indeed, transition metal substituted polyoxometalates (TMSPs) represent a huge sub-class of POM-based materials and have been widely explored due, in large part, to the ability of POMs to stabilise high valent metal ions, afford robustness to harsh reaction conditions under which most organic ligands decompose, and support the formation of large, polynuclear metal complexes between discrete POM ligands. Furthermore, it has also been shown that the introduction of specific TM cations (*e.g.*, Cr^{3+}, Ni^{2+}), Lanthanides (*e.g.*, Ce^{3+}) or main-group cations (*e.g.*, Sn^{2+}) into the POM framework can be used to activate the resultant systems to visible light.[21, 22] Further discussion on TMSPs is beyond the scope of this article, but has been extensively covered in other recent review articles.[23, 24]

ii) Cation exchange: As polyanions, POMs are necessarily isolated with charge-balancing cations. These can be specifically selected to bestow desirable properties and are easily exchangeable with other inorganic or organic cations. In particular, tetra-*n*-butylammonium (n-Bu_4N^+) or similar organic cations are often added to solubilise POMs in organic solvents. Cationic dyes and photosensitizers have also been employed to increase absorption in the visible region,[25, 26] and the resultant salts are typically classified as class I organic-inorganic hybrid POMs. Key examples of such visible-light photosensitive POM systems are given in Section 2.1, and further examples can be found in the recent literature.[26-31]

iii) Covalent Modification: POMs modified with organic or organometallic moieties are typically obtained through two routes, involving either addition of organic or organometallic species to the vacant site or sites on a lacunary POM or by reaction of an organic species with the terminal oxygen atoms of addenda atoms to form covalent bonds. These systems can be described as Class II organic-inorganic hybrid POMs, and have been the focus of a number of excellent review articles in recent years, due to their diverse structural features and potential applications in a range of technologies.[16, 19, 32] These systems represent the core focus of this *Perspective*, and are discussed in detail in Section 2 below.

1.3. Fundamentals of Polyoxometalate Photochemistry

The photoactivity of POMs has been extensively studied over the past few decades.[33-35] All POM clusters typically show strong absorption maxima with high molecular absorption coefficients ($\varepsilon > 1 \times 10^4\ M^{-1}\ L^{-1}$) centred in the UV region of the spectrum due to the presence of O → M ligand-to-metal charge transfer (LMCT) absorption bands, localised on the terminal oxygen positions of each addenda metal centre. Often, 'tailing' of the LMCT band absorptions into the visible region can be observed, especially for vanadate and molybdate POMs. Absorption into the O → M (LMCT) band typically gives rise to the characteristic colourless or pale yellow/orange colouration of most POMs and targeted excitation of this band is the basis for the inherent photo-activity of all POM clusters. In this *Perspective*, we term the UV-photoexcitation of POMs as a *UV-endo* process because the photo-induced charge separation is centred entirely on the POM core (*endo* = internal; from inside). The *UV-endo* mechanism can be defined as follows (Scheme 1):



Scheme 1. The *UV-endo* charge separation mechanism, in which the photo-induced charge separation is centred entirely on the POM. Here, excitation into the O→M ligand to metal charge transfer (LMCT) band (localised on the terminal W=O groups of the POM core) leads to reduction of the metal centre and formation of a highly reactive oxo-radical species. Oxidation of a substrate, *S*, often *via* hydrogen-atom abstraction leads to quenching of the charge separated state and trapping of an electron on the POM core. Subsequent oxidation of the POM core can be used to regenerate the d^0 ground state.

Here, absorption of UV light into the LMCT band promotes an electron from a spin-paired, doubly occupied highest occupied molecular orbital (HOMO) involved with bonding (typically an oxygen 2p orbital) to the antibonding, lowest unoccupied molecular orbital (LUMO, which is typically a metal d orbital). This generates a localised d^1 electron on the metal centre and an oxo-centred radical, where the short-lived photo-excited triplet state species will readily oxidise a range of substrates. When the charge separated (CS) state is quenched (*via* a proton-coupled electron transfer from the substrate to the oxo-radical cation, for instance), the trapped d^1 electrons give rise to visible light absorption through a newly formed $M^{(n-1)+} \rightarrow M^{n+}$ intervalence charge-transfer (IVCT) band, such that mixed-valence POMs of this type display intense blue colour (historically referred to as “heteropoly blues”).

The inherent light-induced photoredox activity of POMs, coupled with their rich, reversible redox properties, leads to wide-ranging reactivity, and as a result they have been employed in a variety of both heterogeneous and homogeneous oxidation and reduction reactions.[22] Indeed, POMs are ideal candidates for the complex, multi-step photoredox-systems required in solar fuel applications,[36] due to the high number of redox-accessible metal centres present and the negligible structural perturbation associated with the redox processes, leading to robust, highly reversible, multi-redox properties. A key limitation however, remains the ease with which the POM photocatalyst can be re-oxidised (thus closing the catalytic cycle) where re-oxidation of the reduced POM species is typically achieved by the use of molecular oxygen or hydrogen peroxide.

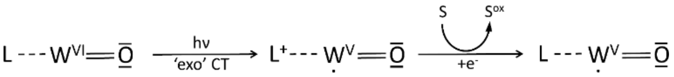
It was not until the early 1980s that the systematic study of photocatalysis by polyoxometalates became a mainstream topic and was pioneered by, amongst others, Hill, Papaconstantinou, Yamase and their coworkers.[4, 33, 37] These works have been extensively reviewed in the literature, but briefly it should be noted that these initial studies focussed mainly on three POM clusters, *i.e.* derivatives of the Keggin-type $[XM_{12}O_{40}]^{n-}$ and the Dawson-type $[X_2M_{18}O_{62}]^{n-}$ heteropolyoxometalates, respectively with M = W, Mo; X = Si, P, S, *etc*. and the decatungstate ion $[W_{10}O_{32}]^{4-}$. Thanks to their attractive combination of properties (stability, solubility, redox chemistry, etc.), these particular clusters have been shown to be ideal systems for advancing POM photochemistry. The decatungstate anion in particular has proven to be an effective photocatalyst for C-H activation reactions,[38-40] a wide range of organic oxidations,[41, 42] and even fluorination processes.[43]

Despite these advances, the more widespread uptake of POM photochemistry has been restricted by the energy of the POM-centred O→M LMCT band, which usually falls well within the UV region of the spectrum (typically at wavelengths of 300 – 330 nm). Recently however, new approaches to POM photochemistry, which target visible-light photo-sensitization *via* secondary chromophores or direct manipulation of the POM-based LMCT character, allow the favourable properties of the POM cluster to be exploited in new photochemical systems designed with sustainability in mind. In particular, hybrid POM chemistry has proven crucial to the growth of this field and this *Perspective* will highlight the key molecular design approaches, photo-activation strategies and potential applications, addressing the past, present and future of this burgeoning field.

2. Photochemistry in Hybrid Polyoxometalates

Hybrid POMs have rapidly become prominent in the field of visible-light POM photochemistry because they allow an effectively limitless range of different organic and organometallic functionalities to be combined with the polyoxometalate core into discrete molecular ensembles. These multi-functional hybrid clusters can - in principle at least - be constructed through careful molecular design, allowing their intrinsic chemical and physical properties to be tailored to meet an extraordinarily wide-ranging array of specific requirements. Recent examples have shown the potential of this approach across a broad variety of different applications, encompassing interests as diverse as biotechnology and medicine,[44, 45] catalysis[10, 16, 22] and supramolecular design.[46-48]

In comparison to the conventional means of POM photo-excitation described above (which we termed the *UV-endo* mechanism), hybrid POMs have found enormous utility in photochemical applications because they allow secondary chromophore species to be combined with the POM cluster, generating photoactive dyads in which the absorption characteristics can be controlled by selection of an appropriate visible-light-active photosensitizer. This approach, which we describe herein as the *vis-exo* mechanism (*exo* = external; from outside), thus differs from the traditional *UV-endo* approach in that it relies on either an inter- or intra-molecular charge transfer process between a distinct sensitizing species (L) and the POM cluster (Scheme 2). Here, charge transfer between the high-energy photoexcited state on the chromophore and the POM cluster leads to the formation of a short-lived charge separated state, with the hole localised on the chromophore and the electron on the now-reduced POM core. Efficient quenching of this state, most commonly through reaction with a suitable sacrificial reductant, leads to charge trapping/accumulation on the POM and regeneration of the sensitizer ground state:



Scheme 2. The *vis-exo* charge separation mechanism, in which photo-induced charge separation occurs between an oxidised photosensitiser and a reduced POM. Here, photoexcitation of a chromophore, *L*, leads to charge transfer from the excited state on the sensitizer to an electrostatically or covalently bound POM core. A sacrificial oxidant, S, is used to quench the charge separated state, preventing charge recombination and trapping an electron on the POM core.

To date, this *vis-exo* strategy has been used to creatively explore a range of photo- and electro-chemical applications, including in non-linear optical materials,[49-51] the design of unusual fluorescent probes,[52, 53] photovoltaics,[54-56] photochromic materials,[53, 57-59] and, most prominently, artificial photosynthesis and the generation of solar fuels.[60, 61]

2.1. Considerations in Hybrid-POM Classification

Fundamentally, there are two well-recognised classes of hybrid POM species which are defined by the specific nature of the interaction between the POM and organic/organometallic components.[62] Class I hybrids are those in which the organic or organometallic moieties are associated with the POM *via* weak interactions, whereas class II hybrids are those in which covalent bonds are used to graft functional moieties directly to the POM cluster. In a photochemical sense, both classes ofhybrid compounds have generally exploited similar strategies to effect photo-sensitization of the polyoxoanion component in the visible regime, whereby an 'exo' charge transfer process (as above) from one or more associated chromophore species is used to drive reduction of the POM (and concomitant oxidation of the chromophore). Several excellent recent reviews have covered class I hybrids in detail and should be referred to for a more in depth discussion of these materials and their applications.[30, 35] It is nevertheless useful to briefly highlight some of the key features of class I hybrid compounds and their relative merits and weaknesses in comparison to the more synthetically demanding class II hybrid compounds.

In essence, class I organic-inorganic hybrid POMs encompass any polyoxoanion which is closely associated with organic or organometallic moieties *via* non-covalent electrostatic, hydrogen-bonding or van der Waals interactions. Often, preparation of these materials requires little more than simple cation metathesis and it has therefore become an attractive and relatively facile method to prepare photo-active hybrid materials. In this context, the most common approach involves the formation of a charge transfer salt between the POM cluster and a suitable cationic sensitizer complex, of which Ru-polypyridyl complexes are by some distance the most frequently employed (as originally pioneered by the work of Balzani, Anson, Hultgren, Keyes and their respective co-workers).[63-66] More recently this strategy has garnered considerable interest in the field of water oxidation, where the work of Hill and Bonchio in particular, has demonstrated how catalytically active transition metal substituted POM clusters can be sensitized in the presence of the $[Ru^{II}(bpy)_3]^{2+}$ chromophore and a sacrificial oxidant in order to drive the oxidation of water under visible light irradiation.[67-71] Interestingly, the same approach can also be used to drive the corresponding hydrogen-reduction half-reaction,[72, 73] and new studies have even shown how this strategy can be combined with supramolecular, self-assembly and materials design approaches to generate next-generation photocatalytic porous framework materials,[74, 75] which may help to mitigate some of the more common disadvantages of class I hybrids, discussed below.

Whilst class I photoactive hybrids continue to remain a topical area of study, they have long been known to have several key weaknesses. Firstly, whilst the electrostatic association between the polyoxoanion and cationic sensitizers is often reasonably strong (with formation constants frequently in the range of $10^5 - 10^7$),[30] this class of materials is highly susceptible to changes in the solution conditions (ionic strength, competitive interactions with other cationic or hydrogen-bonding species, pH changes, etc.). Moreover, the optical properties of these complexes are often strongly dependent on the specific stoichiometry, binding geometry and orbital overlap interactions between the POM and chromophore, factors which are neither predictable nor necessarily easy to control. Most importantly perhaps, and certainly from a more forward-looking standpoint, are the inherent limitations imposed on the molecular and supramolecular design of new hybrid POM clusters or assemblies by adopting an electrostatic-only approach. In other words, whilst class I hybrids may be simple to synthesise and screen for attractive properties, it comes at the cost of a lack of control over the precise interactions between the POM and sensitizer components and a significantly curtailed ability to further engineer additional attractive chemical and physical properties into the resulting complex (i.e. solubility, supramolecular assembly, surface interactions, etc.).

Though class II hybrid POMs are considerably more demanding to synthesise as a result of their added complexity, covalent attachment of photosensitizing moieties has several distinct advantages which will be discussed in the context of some of the more relevant recent examples from the literature. Notably, whereas there is no particular limit on the type of polyoxoanion structures which can form class I complexes, even a cursory glance at the current literature reveals several key structural archetypes which form the basis for the overwhelming majority of covalent hybridisation strategies. Briefly, these include derivatives based on the $[M_6O_{19}]^{n-}$ Lindqvist anion (where M = V, Mo), the $[XM_6O_{24}]^{n-}$ Evans-Anderson anion (where X = Mn, Fe, Cr, I, Te, etc.; and M = Mo, W) and a variety of lacunary or metal-substituted derivatives of the $[XM_{12}O_{42}]^{n-}$ Keggin or $[X_2M_{18}O_{62}]^{n-}$ Wells-Dawson anions (where X = P, Si and M = W) (Figure 3). The ever-expanding scope of hybridisation/functionalisation in each of these structure-types is beyond the scope of this *Perspective*, however there are several comprehensive reviews which explore their synthesis and properties in greater detail.[19, 76, 77]

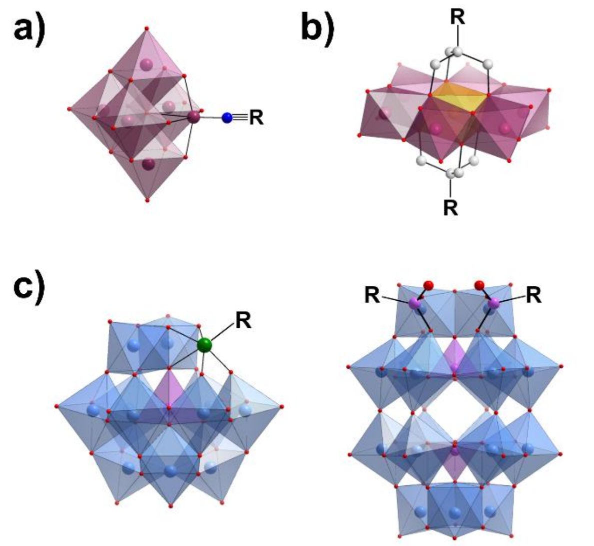


Figure 3. Archetypical organic-inorganic hybrid POM clusters and functionalization modes, showing: a) the imido-functionalised Lindqvist anion; b) *bis*-triol-functionalised Anderson anion; c) organotin-functionalised Keggin anion, and; d) *bis*-organophosphonate-functionalised Dawson anion (note that methods to functionalize Keggin- and Dawson-type anions are generally interchangeable). Colour code: {MoO_6} = plum polyhedra; {WO_6} = blue polyhedra; {XO_6} = orange polyhedra; {XO_4} = purple polyhedra; Mo = plum; Sn = green; P = purple; O = red, C = grey; N = blue. Cations are omitted for clarity.

2.2 *Vis-exo* photoexcitation in class II hybrid materials

By far the most common method of visible light photo-sensitisation in hybrid POM photochemistry is inter- or intra-molecular charge transfer from an associated/appended chromophore to the POM cluster, which then serves as an electron reservoir or relay, depending on the desired application. This approach is an obvious parallel with that pioneered in dye-sensitized solar cells,[78] where a suitable sensitizer is used to inject charge into the semi-conducting layer (in this sense, the HOMO and LUMO frontier orbitals of the POM are loosely comparable to the valence and conduction bands of the semi-conductor, respectively). In general, the key considerations in any such system have tended to involve how the charge separation and recombination lifetimes can be controlled and how the material properties of the dyad can be tailored to prevent deleterious self-aggregation and quenching behaviour. In addition, it should also be possible to tailor the material properties to the envisaged application (i.e. in homogeneous or heterogeneous catalysis, surface deposition or integration with electrode materials etc.).[18] Covalent hybridisation provides an excellent opportunity to control these properties at the both the molecular and supramolecular levels, and recent studies over the past decade or so have helped to greatly expand the scope and ambition of this burgeoning area of study. The following discussion will aim to provide a broad overview of this work and highlight key observations, with a view to the design and application of future photo-active hybrid materials.

One of the earliest examples of the assembly of covalent POM-photosensitizer hybrid complexes was reported by Bonchio *et al.* in 2004, where the divacant lacunary silicotungstate [γ-$SiW_{10}O_{36}$]$^{8-}$ was coupled with organosilane-functionalised C_{60}-fulleropyrrolidine units.[27] The resulting hybrid clusters were employed in the heterogeneous, visible-light driven photo-oxidation ($\lambda > 375$ nm) of phenol and an organic sulfide in water under 1 atm O_2. In the oxidation of phenol, benzoquinone was identified as the only product with an average conversion of *ca.* 90 % and a turnover number (TON) of *ca.* 50 after 150 mins reaction time. Analogous hybrid POM clusters synthesised without the C_{60} groups were found to show no photocatalytic activity whilst the photo-sensitized hybrid was generally found to be both more robust and more efficient in comparison to electrostatically formed photo-active POM adducts. Importantly, variation in the length and structure of the linking chain between the POM and C_{60} sensitizers had a profound effect on the stability and thus catalytic performance of the complex, providing an early example of the importance of careful design in the preparation of the hybrid material.

2.2.1. Mechanistic considerations in *vis-exo* charge-transfer

Whilst the role played by the tungstate cluster in the photochemical properties of the hybrid-assembly was not discussed in detail in this early work, subsequent studies have explored the nature of the charge transfer interactions between the sensitizing species and the POM. For example, closely following Bonchio's initial study, Peng and co-workers reported the preparation of a series of POM-grafted hybrid polymer materials, where imido-derivatized [$Mo_6O_{19-x}(N{\equiv}R)_x$]$^{2-}$ (x = 1, 2) Lindqvist-type anions were directly incorporated into π-conjugated polymer chains.[79, 80] In these systems, the specific properties of the organic linker was found to play a significant role in the photochemical properties of the hybrid aggregates. When a rigid π-conjugated bridging species was used to couple the POM unit with the polymer backbone the fluorescence was effectively quenched, indicating efficient charge transfer between the photo-excited state of the polymer and the pendant {Mo_6} anions. Conversely, the use of a flexible non-conjugated linker resulted in a four-fold increase in the fluorescence quantum yield, strongly suggesting that *through-bond* photo-induced electron transfer is the dominant mechanism in this type of hybrid (Figure 4a).[79] Moreover, titration of discrete {Mo_6} was found to have little effect on quenching the polymer emission, again highlighting the importance of the covalent functionalization step. Subsequently, the authors prepared hybrid-polymer films for use in photovoltaic applications where the acceptor properties of the hexamolybdate units (coupled with efficient charge transfer between the hybridized organic and inorganic components) are used to form longer-lived charge-separated states and improve the number of available free charge carriers in the polymer during photo-irradiation, resulting in improved device performance.[80] Recent work has shown that a hybrid polymer film comprised of bis-functionalized imido-hexamolybdate anions copolymerized with imide-functionalized napthodithiophene-based monomers shows a 24-fold increase in power conversion efficiency (PCE) under solar irradiation over the comparable non-hybrid polymer. This

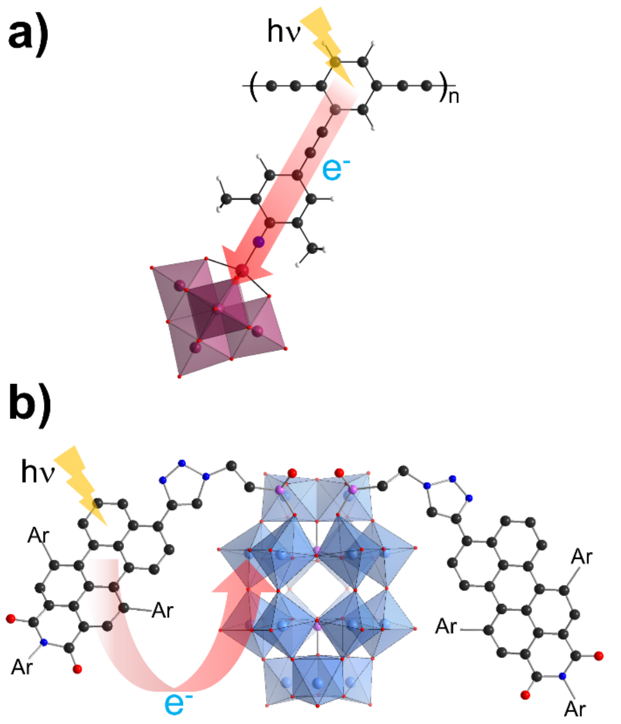


Figure 4. The different charge transfer mechanisms observed in the *vis-exo* photoexcitation of hybrid POM dyads, showing: a) the through-bond charge transfer mechanism, in which charge is transferred predominantly through conjugated bonds (see ref. 79 for example), and; b) through-space charge transfer, whereby charge transfer relies on close-contacts between the electronically isolated sensitizer and POM units (see ref. 81 for example).

is largely thanks to an increase in the short circuit current density arising as a result of the efficient charge separation between the polymer chain and the POM clusters.[82]

In contrast to the through-bond approach used in organoimido-functionalized Lindqvist-type hybrids,[83] an elegant series of studies in 2009 by Odobel, Meyer and Harriman *et al.* highlighted the importance of the competing *through-space* charge transfer mechanism by functionalizing a mono-lacunary $[P_2W_{17}O_{61}]^{10-}$ anion with organosilane and organophosphonate tethered perylene-monoimide or zinc (II) tetraphenylporphyrin (ZnTPP) derivatives (Figure 4b).[81, 84] In doing so, they discovered that the ability of the POM to quench the S_1 state emission of the chromophore was directly related to the "flexibility" of the linker group (where ∠ P···P–C is generally greater than 160° and the corresponding ∠ Si···Si–C is *ca.* 135°). Unlike conventional through-bond approaches, where rigid well-defined systems are generally preferable, those hybrid dyads with the greatest structural flexibility were found to display the most efficient charge transfer behaviour (for example, the perylene S_1 emission has a quantum yield of 0.02 in the phosphonate-hybrid and 0.35 in the equivalent siloxane). In these hybrids the somewhat complex photodynamics are explained by the formation of several conformers, as determined by pressure-dependent fluorescence measurements, each of which has a different rate of charge separation and recombination. Thus, although there is a favourable thermodynamic driving force for the intramolecular charge transfer (note that phosphonate hybrids also typically show greater stabilization of the LUMO than siloxane systems), the through-space mechanism is found to predominate in these non-conjugated systems, as is often the case in hybrid-POM species. This is a result of the largely insulating character of the linker units employed (here, as in many cases, the POM and chromophore units can be demonstrated *via* electrochemical and spectroscopic measurements to be electronically well-isolated) and indicates the importance of considering both charge- and mass-transfer dynamics when attempting to design new photo-active hybrid-POM species.

2.2.2. Molecular design considerations and early progress towards photochemical applications

Whilst early work in the field helped to shed light on the nature of the inter- and intra-molecular charge transfer dynamics between the sensitizing moieties and the POM, more recent work has explored how the structure of the chromophore and nature of the POM cluster itself can be tailored towards more effective charge transfer properties and, more importantly, specific applications. For example, the hybrid complexes described above, originally reported by Odobel, Meyer and Harriman, are amongst the first where charge accumulation is demonstrated on the metal-oxide surface under steady-state visible-light irradiation (whilst in the presence of a sacrificial reductant, such as an amine or alcohol). Here, the POM can be fully reduced by one electron under irradiation at $\lambda > 400$ nm, however, despite a favourable driving force (the Dawson-anion can be electrochemically reduced by two electrons before formation of the porphyrin π-radical, for instance), it was not possible to drive the POM to a $2e^-$ reduced state due to a rapid charge-shift reaction between the sensitizer and the mono-reduced POM. This is significant from an application point of view as a key goal is the generation of fuels such as H_2 or CO *via* solar irradiation, all of which are multi-electronic processes which are facilitated in nature by charge accumulation on the appropriate reaction centre.[85] To overcome this issue, Harriman, Odobel *et al.*, extended their earlier work by grafting multi-porphyrin assemblies containing ZnTPP-based donors and a free-base porphyrin intermediate to help promote directional charge transfer and prevent rapid charge recombination between the POM and ZnTPP donors (Figure 5).[86] In the presence of a sacrificial reductant, which acts to quench the oxidized π-radical cations of both the ZnTPP and free-base porphyrin units before charge recombination can occur, slow 2e- reduction of the POM unit was successfully observed.

It should also be noted that both the nature of the POM cluster (or archetype) used as a platform to support the hybrid complex, and the specific type of linker used to tether the chromophore to the polyoxoanion, are critically important in determining the photophysics of the resulting dyad. This is not only in terms of the expected charge transfer mechanism (i.e. through-space or through-bond) but on whether effective charge transfer can be expected to occur at all. A recent theoretical analysis of porphyrin-functionalized Keggin-, Lindqvist- and Anderson-type hybrids neatly encapsulates this concept, showing how the

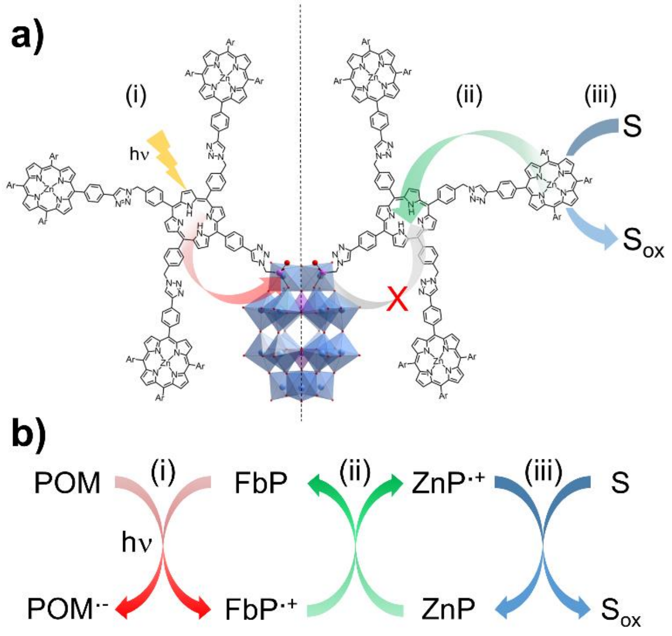


Figure 5. a) The bio-inspired multi-porphyrin functionalised Dawson hybrid reported by Harriman, Odobel *et al.*,[86] and; b) the photo-induced electron transfer pathway involving: (i) photoexcitation and charge transfer from the free-base porphyrin (FbP) to the POM core; (ii) quenching of the hole formed on the FbP by secondary charge transfer from the metallated Zn-porphyrin (ZnP), thus preventing charge recombination between POM$^{\cdot-}$ and FbP$^{\cdot+}$, and; (iii) oxidation of a sacrificial electron donor, quenching the hole on ZnP and thus trapping an electron on the POM cluster. Repeated photo-excitation allows transfer of a second electron to the POM unit, facilitating multi-electron charge accumulation. Adapted from ref. 86 with permission from the PCCP Owner Societies

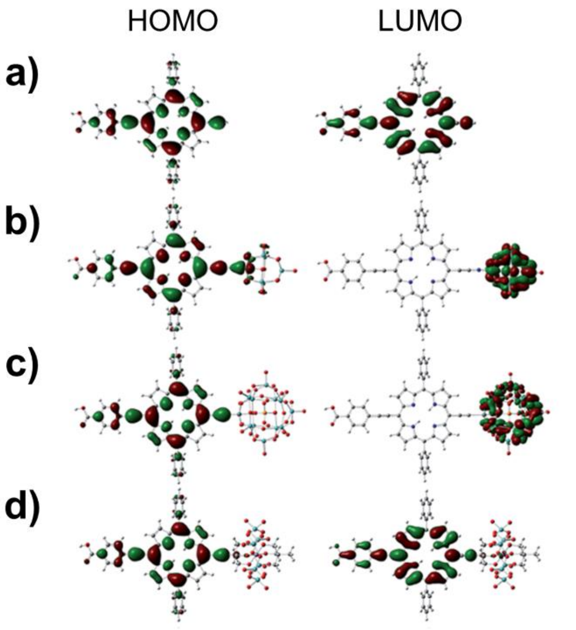


Figure 6. Simulated frontier orbital distributions for the free chromophore: a) 1-carboxyphenyl-10-ethynyl-5,15-biphenyl-porphyrin and its hybridised products with: b) the imido-functionalised {Mo$_6$}-Lindqvist anion; c) the stannane-functionalised {PMo$_{11}$}-Keggin anion, and; d) the *bis*-triol-functionalised {MnMo$_6$}-Anderson anion. Whereas excitation into the LUMO state is shown to result in clear charge transfer to the POM core in the case of (b) and (c), the Anderson derivative is shown to have almost no effect on the frontier orbital distribution of the free chromophore, highlighting the dependence of the charge transfer dynamics on the nature of the functionalised POM anion. Adapted from ref. 87 with permission from the Royal Society of Chemistry.

distribution and energy of the frontier orbitals in the resulting hybrid complexes is heavily dependent on the nature of the POM/linker.[87] By modelling comparable hybrid clusters based on the grafting of an ethynyl-tethered porphyrin derivative to either an imido-functionalized {Mo$_6$} anion, a stannane-functionalized {PMo$_{11}$} anion or a (bis-)tris-alkoxide-functionalized {MnMo$_6$} cluster, the authors show that the absorption profile and charge transfer character of the hybrid dyads varies dramatically depending on the POM cluster present. For instance, both the {Mo$_6$}- and {PMo$_{11}$}-based hybrids are found to have well-defined HOMO and LUMO states localised on the porphyrin sensitizer and the polyoxoanion, respectively, whereas in the {MnMo$_6$}-based Anderson complex the POM unit is found to have almost no effect on the frontier orbitals of the porphyrin moiety so that the photoexcitation process takes place entirely on the organic component (Figure 6). It is also important to note that the Lindqvist hybrid shows a significant red-shift (*ca.* 100 nm) in the simulated absorption spectrum whereas introduction of the Keggin or Anderson clusters has little to no effect on the absorption profile of the chromophore. This effect presumably arises as a result of the enhanced orbital overlap in the Lindqvist hybrid as a result of the direct integration of the sensitizer with the polyoxoanion through the imido-linker, highlighting the importance not just of the POM cluster but also the specific linker unit in governing the charge transfer properties of the hybrid complex.

These trends in the photo-chemical properties of hybrid-POM clusters based on different parent anions have also been elucidated experimentally. A comparison of the tris-alkoxy functionalized {MnMo$_6$O$_{24}$} Anderson and [P$_2$W$_{15}$V$_3$]$^{9-}$ modified Wells-Dawson clusters, each with appended ZnTPP groups, shows dramatically different photophysical behaviour.[88] Each hybrid complex possesses an identical linker configuration and displays no significant electronic communication in the ground state. In both cases, the Gibbs free energy for the charge transfer are favourable however, whilst the Dawson-type acceptor almost fully quenches the luminescence of the ZnTPP chromophore (reducing the quantum yield by up to 97 %), the Anderson-based analogue shows no quenching behaviour at all; an observation the authors attribute to heavy and paramagnetic atom effects.

Further work by the authors showed that the Dawson-type hybrid could be employed as the key component in the first example of a photo-active POM-modified electrode forphotovoltaic applications.[54] Here, the hybrid complex is self-assembled onto an indium-tin-oxide (ITO) electrode and acts as an effective photo-sensitizer and electron relay functioning in a bio-inspired, electronically downhill cascade process using the I$_3^-$/I$^-$ redox couple as a redox mediator (Figure 7).

In line with the studies reported above, Anderson-type POMs are generally considered to be poorly suited to

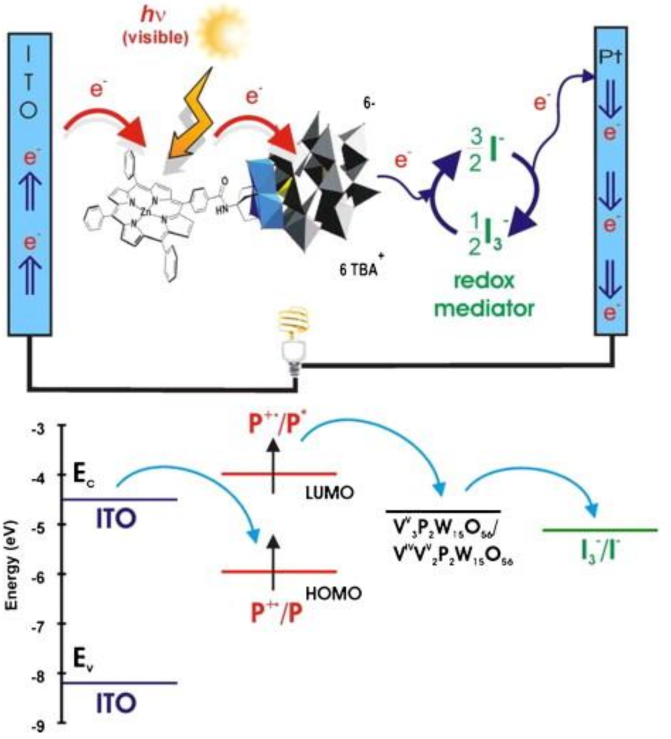


Figure 7. Representation of the hybrid-POM modified electrode (top) reported by Hasenknopf, Ruhlmann *et al.*, showing a schematic of the photo-electrochemical charge transfer process and the corresponding energy levels of each component in the hybrid-POM-mediated charge transfer cascade (below). Reproduced from ref. 54 with permission from Elsevier.

photochemical applications,[30] due in large part to their limited redox properties (where it is generally accepted that Anderson-clusters do not share the pseudo-reversible multi-redox chemistry associated with other POM archetypes, such as the Keggin or Dawson anions). In fact, several successful examples of hybrid-Anderson dyads have recently been reported. For instance, Hasenknopf, Ruhlmann *et al.* have demonstrated the use of tris-alkoxide ligands as a means of functionalizing Anderson-type POMs for visible light driven photochemical applications. Whilst early work was unsuccessful in generating robust photo-active dyads,[89] a follow-up approach using the electropolymerization of bis-pyridyl functionalized $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(p\text{-}C_5H_4N)\}_2]^{3-}$ clusters with zinc octaethylporphyrin (ZnOEP) found greater success.[90] Here, total quenching of the porphyrin emission was observed indicating efficient charge or energy transfer to the POM core. To explore their reactivity, irradiation ($\lambda > 385$ nm) of the polymer films in the presence of propan-2-ol (as a sacrificial reductant) and Ag_2SO_4 as the substrate was used to synthesise a variety of Ag^0 nanostructures, using the POM as a photo-activated reductant. Control experiments performed on solutions of isopropanol and Ag_2SO_4 in the absence of the hybrid polymer catalyst were found to reduce Ag^+ at a mere tenth of the rate and the resulting particles were shown to have markedly different topologies in the absence of the polymer matrix acting as both catalyst and template.

2.2.3. Multi-electron charge accumulation and solar fuel production

One of the key themes which has emerged from the study of hybrid-POM systems for photochemical applications is their exciting potential as multi-electron charge accumulators and/or charge transfer catalysts. This is a key requirement in the design of any future photocatalyst for the renewable generation of so-called solar fuels such as H_2 and CO,[91, 92] which could conceivably help to replace our current dependence on fossil fuels for transportation, manufacturing and as chemical feedstocks. A recent, landmark series of studies by Proust, Izzet *et al.* has shown how an elegant approach to molecular design could be used to ultimately facilitate persistent multi-electron charge accumulation and photocatalytic H_2 evolution in a cyclometalated hybrid-POM complex.[60, 93-96] Utilizing a post-functionalization approach to modify organotin- and organosilyl-tethered $[SiW_{11}O_{39}]^{7-}$ Keggin or $[P_2W_{17}O_{61}]^{10-}$ Dawson clusters appended with a pendant alkynyl group, the authors successfully introduced a heteroleptic Ir(III)-chromophore *via* Sonogashira cross-coupling.[95, 96] Whilst electrochemical measurements show that the POM and Ir-complex are electronically distinct in all cases, as could be expected in these hybrids (see above), photo-physical measurements show the existence of a short- lived Ir-centred excited state followed by a long-lived charge separated state (in the order of hundreds of ns) comprising the reduced POM and oxidized chromophore. The rate of charge transfer in the four hybrid clusters studied closely follows the same trend observed in the redox behaviour of each, where the most easily reduced species (the siloxane-functionalized Keggin anion) shows the most favourable thermodynamics for both charge separation and charge recombination processes (*i.e.* it is both a better donor and acceptor). The key breakthrough is revealed by TD-DFT analysis however, which shows how the heteroleptic structure of the chromophore significantly improves the rate of charge transfer relative to charge recombination. The lowest lying excited state is formed on the picolinate component, which then undergoes intramolecular charge transfer to the LUMO state on the POM whereas, crucially, the reverse process proceeds *via* charge transfer from the POM to the more distant phenylpyridine ligands (Figure 8a). As the overlap between the wavefunctions of the donor and acceptor groups can be expected to fall exponentially with distance, the heteroleptic nature of the chromophore leads to $k_{CS} >> k_{CR}$ and is responsible for generating directionality in the nature of the charge-transfer process. This is a significant departure from previous systems where the structure of the chromophore leads either to a lack of directionality or, worse still, reversed directionality where $k_{CR} >> k_{CS}$.

Based on these results, the authors proceeded to study the siloxane-functionalized Dawson-Ir hybrid as it offered the best balance between charge separation efficiency and the lifetime of the charge separated state.[60] Steady-state illumination of the hybrid-complex (400 nm > λ > 800 nm) performed in *N,N'*-dimethylformamide (DMF) in the presence of triethylamine as a sacrificial reductant showed rapid reduction of the POM core to the 1e$^-$ reduced state ($\tau_{1/2}$ = 43 s, ϕ_{400nm} = 10.5 ± 1.0%; where $\tau_{1/2}$ = the half-reaction time constant and ϕ_{400nm} = quantum yield at 400 nm) followed by a concurrent but slower second reduction to the 2e$^-$ reduced cluster ($\tau_{1/2}$ = 270 s, ϕ_{400nm} = 2.3 ±0.5%) (Figure 8b). This is explained by considering the lower thermodynamic driving force (i.e. more negative redox potential) of the $\{P_2W_{17}\}$ cluster's 2nd reduction step. Given the well-known proton-coupled electron transfer behaviour of POM clusters,[98] acetic acid was added to the photolysis solution and this was found to lead to a dramatic reduction in the rate of the 2nd photo-reduction particularly ($\tau_{1/2}$ = 60 s). This can be correlated to the significant positive shift observed in the POM's 2nd reduction wave upon addition of acid, again providing evidence of the sensitivity of charge-transfer kinetics to the redox properties (or in other words, energy of the LUMO state) of the POM. Most remarkably, when a solution of the hybrid-POM catalyst, TEA (sacrificial reductant) and acetic acid (proton source) are subjected to steady-state illumination over a period of 7 days, headspace GC analysis revealed constant – albeit slow – evolution of H_2 gas with a turnover frequency (TOF) of ca. 0.25 h^{-1} and a maximum turnover number (TON) of 41 (Figure 8c). Crucially, no H_2 was evolved in the absence of either TEA or when a reference POM-hybrid containing no photosensitizer was used. Furthermore, only trace H_2 was evolved from the discrete heteroleptic Ir-complex and an analogous electrostatically bound hybrid evolved H_2 at half of the rate of the covalent dyad.

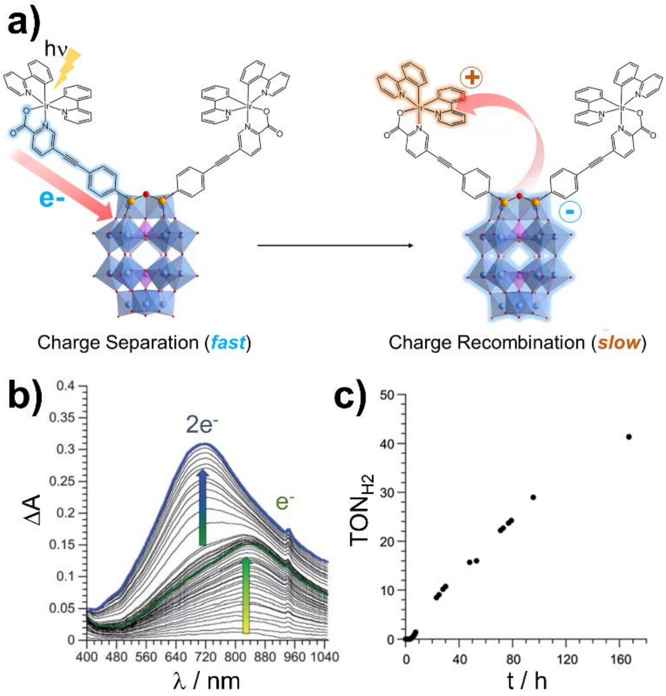


Figure 8. a) The charge separation and recombination steps in the cyclometalated hybrid POM cluster reported by Proust, Izzet *et al.*; b) time-dependant absorption spectra illustrating the growth of POM-based IVCT bands corresponding to the trapping of two electrons on the POM core, and; c) hydrogen evolution upon introduction of TEA (sacrificial reductant) and acetic acid (proton source) during steady-state illumination over a period of 7 days. Adapted from ref. 60 with permission from The Royal Society of Chemistry.

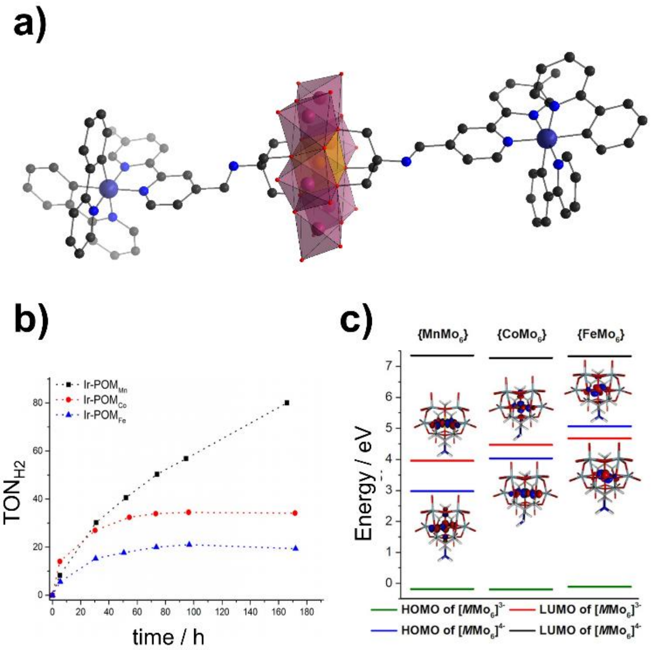


Figure 9: a) Structure of the Iridium-functionalised Anderson-type hybrid POM reported by Streb, Rau and coworkers; b) hydrogen evolution catalysed by hybrids containing different central heteroatoms (Mn = black, Co = red, Fe = blue), and; c) frontier orbital energies of the hybrid clusters, where the heteroatom is in either an M^{II} or M^{III} oxidation state, as determined by DFT calculations. Colour code: $\{MoO_6\}$ = plum polyhedra; $\{MO_6\}$ = orange polyhedra (M = Mn, Co or Fe); O = red, C = grey; N = blue. Cations are omitted for clarity. Adapted from ref. 97 with permission of John Wiley and Sons.

This result is therefore hugely encouraging and the pursuit of new hybrid-POM photocatalysts is an ongoing area. One set of notable examples worth highlighting here are a related series of hybrid-clusters derived from the well-known $[Re(CO)_3(bpy)(S)]$ (where bpy = bipyridine, or a derivative thereof and S = solvent) complex.[99, 100] This species is of particular interest for photocatalytic CO_2 reduction and several recent results have begun to explore the photophysical properties of Re-appended hybrids based on Keggin, Dawson or Lindqvist type clusters,[101-103] following the earlier work of Neumann and Poblet, Graff *et al.*, who have studied photochemical CO_2 reduction in an ionically bound $NaH[SiW_{11}O_{39}][Re(\mathbf{L})(CO)_3(S)]$ (**L** = 15-crown-5-phenanthroline; S = CH_3CN, *N,N'*-dimethylacetamide) where the POM unit is capable of acting as a photosensitizer, electron reservoir and electron donor.[104, 105] Further work in this area should be of considerable interest given the potential for interesting synergistic interactions between the POM, photosensitizer, substrate and – particularly in the pursuit of CO_2 reduction to other useful C_1 feedstocks such as CO, H_2CO, HCOOH, CH_3OH and CH_4 – proton association with the hybrid-cluster.

Very recent work on the photocatalytic evolution of hydrogen was presented by Streb, Rau *et al.*, who synthesised a series of $[MMo_6O_{24}]^{n-}$ Anderson-type hybrids (Figure 9a, where M = Mn, Fe and Co) with appended heteroleptic Ir-chromophores using a similar strategy to Proust, Izzet *et al.* (as above).[61, 97] These hybrid-assemblies are particularly interesting due to their superior H_2 evolution properties and especially so, given that the Anderson cluster is not always considered to be an especially effective electron reservoir for charge accumulation. Here, all of the hybrid-complexes show some residual emission from the Ir-chromophore, indicating somewhat inefficient charge transfer (particularly in comparison to similar Keggin- or Dawson-type hybrids). Furthermore, the effectiveness of the quenching is highly sensitive to the type of central heterometal present and correlates extremely well with both the experimental and theoretical redox potential of the metal, where Mn >> Co > Fe (Figure 9c), *i.e.* a thermodynamic driving force argument can be made for the effectiveness of the charge transfer. When solutions of the hybrid catalyst, triethylamine and acetic acid are irradiated with a monochromatic light source (LED, λ = 470 nm) in dry, degassed DMF, headspace analysis confirms the evolution of H_2 with a TON of 80 over 7 days in the case of the best performing $\{MnMo_6\}$-hybrid (TON_{Co} = 34, TON_{Fe} = 20, Figure 9b). Control experiments found that the performance of electrostatically bound analogues dropped off significantly, with a reduction in observed TONs of between 80 and 93 %, whereas no H_2 evolution could be detected in the absence of either the electron or proton donor. Dynamic light scattering measurements and microfiltration was used to rule out the involvement of adventitious colloidal metal particles.

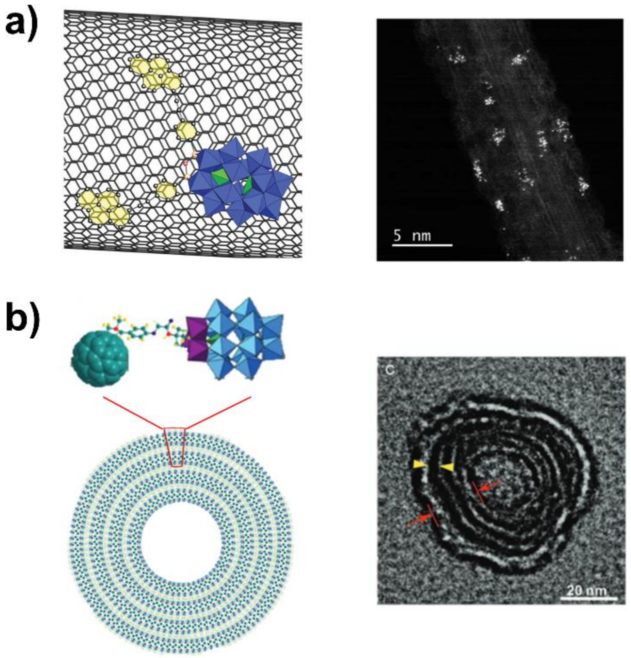


Figure 10: Examples of supramolecular approaches to hybrid POM photochemistry showing: a) surface functionalisation of single-walled carbon nanotubes with a pyrene-appended Dawson cluster (left) and HAADF-STEM imaging of the resultant nanostructures (right), and; b) the formation of 'onion-like' multi-walled micelles using the C_{60}-functionalised $\{P_2W_{15}V_3\}$ Dawson-type cluster (left) and HRTEM imaging of the micellar structure (right). Figure 10a adapted from ref. 106 and Figure 10b adapted from ref. 107 with permission from The Royal Society of Chemistry.

2.2.4. Supramolecular approaches

Lastly, it is useful to note two recent examples of photo-active hybrid-POM materials which show interesting supramolecular behaviours. Proust, Guldi, Marti-Gastaldo and Coronado *et al.* recently reported the synthesis of the $\{P_2W_{17}\}$ Wells-Dawson cluster appended with siloxane-tethered pyrene units (Figure 10a).[106] Interestingly, they exploit the π-π aggregation behaviour of this complex in order to create supramolecular ensembles of the hybrid and single-walled carbon nanotubes (SWCNT). Photophysical measurements show that a new charge transfer interaction is formed between the conventionally electron accepting SWCNT and the hybrid-POM complex with a charge separated state lifetime of *ca.* 2 ns. More recently, Hao *et al.* reported the self-assembly of remarkable 'onion-like' multi-walled micellular structures from a tris-alkoxy tethered $\{P_2W_{15}V_3\}$-hybrid appended with C_{60}-fulleropyrrolidine units (Figure 10b). These amphiphilic complexes form interdigitated bilayers due to the hydrophobic nature of the C_{60} moieties, and the resulting laminar nanostructures are found to be extremely robust to solvent conditions, existing in up to 99 % v/v H_2O:DMSO solutions and tolerating up to 60 % v/v toluene:DMSO before observable decomposition of the micellular structures. As in the work of Bonchio described above, photophysical measurements show that irradiation of the vesicles with green light forms singlet oxygen, which may be interesting for future studies on photodynamic therapy or catalysis.

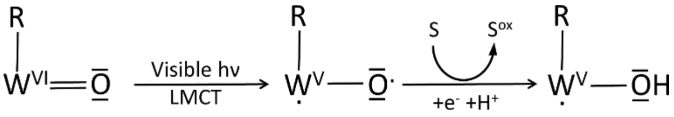
2.2.5 Outlook and perspectives on *vis-exo* photoexcitation

Vis-exo photoexcitation remains the dominant method to photosensitize POM clusters for visible light driven applications and it is our hope that the overview provided above gives a solid introduction to the field. As can be seen above, this strategy has provided a fruitful avenue of exploration in recent years, where expected applications in photovoltaics and photocatalysis (*i.e.* solar fuel production) have attracted the greatest interest thus far. Several key observations emerge from an overview of the field and it is worth briefly summarising them again here. Firstly, it is clear that the complex interplay of different charge transfer dynamics between the sensitizer and the POM are crucial to the photochemical behaviour of the hybrid complex. Whilst these interactions are not always intuitive, a degree of control can be exerted by choice of both POM and linker units, where either through-bond (predominant in Lindqvist-type hybrids) or, more commonly, through-space CT interactions can be mediated by the type and structure of the individual components. Furthermore, improving the lifetime of the charge-separated state has been a long-held goal, though these efforts have frequently been complicated by deleterious charge recombination and self-quenching processes between the reduced POM and the oxidized chromophore. Recently, elegant ligand design – as in the heteroleptic ligands employed by Proust and Streb – has helped somewhat to address these issues, such that it has recently been possible to exploit the acceptor character of the POM core to facilitate multi-electron charge accumulation, facilitating the photocatalytic generation of H_2 from a sacrificial proton donor. This behaviour is particularly crucial in solar fuel applications where evolution of useful fuels or feedstocks (*i.e.* H_2, CO) requires accumulation and concurrent transfer of at least two electrons to yield useful products.

2.3 *Vis-endo* photoexcitation in class II hybrid materials

Very recently, it has been shown that hybridization approaches can also be used to modify the photochemical properties of the POM cluster itself so that it is directly responsive to visible light. Conventionally, only those POM species containing Mo or, more usually, V addenda centres have been shown to have sufficiently low-energy optical transitions to possess any appreciable visible-light photoactivity.[34] In contrast, W-based POMs are almost always found to be inactive under visible-light and rely on either the *vis-exo* sensitization approach discussed above or on irradiation with higher energy UV light (*UV-endo*), as in the case of the well-studied decatungstate photo-oxidation catalyst.[40, 109, 110] Given the superior stability, structural diversity and ease-of-functionalization of polyoxotungstates, new approaches which allow access to the potent photo-reactivity associated with the generation of POM-centred oxo-radicals under visible light are of significant interest, particularly in the context of new photo-catalytic applications.

Conceptually, such an approach would involve modification of the POM in order to access the same *endo* excitation method described above (Scheme 1), where irradiation with visible light could be used to generate the POM-centred charge-separated state (here, we term such an approach *vis-endo* photo-excitation, Scheme 3):



Scheme 3. The *vis-endo* charge separation mechanism. Here, modification of the POM cluster *via* hybridisation with an electron-withdrawing moiety, R, allows visible-light excitation into the POM LMCT band, facilitating the formation of the highly reactive charge separated state found in the *UV-endo* mechanism (see scheme 1). Oxidation of substrate, *S*, often *via* hydrogen-atom abstraction leads to quenching of the charge separated state and trapping of an electron on the POM core. Subsequent oxidation of the POM core can be used to regenerate the d^0 ground state.

Fundamentally, *vis-endo* excitation relies on the 'tail' of the O→M LMCT absorption band of the POM extending into the high energy region of the visible spectrum whilst the absorption maxima remains centred in the UV. As a result, strategies which lower the HOMO-LUMO transition energy – effectively red-shifting the POM LMCT band so as to have sufficient visible light absorption character – are a plausible means to generate new photoactive, functional POM species. Recently, work in our group has shown that the hybridization of the monolacunary $[P_2W_{17}O_{61}]^{10-}$ cluster with 4-carboxyphenyl phosphonic acid can be used to modify both the electro- and photo-chemical properties associated with the polyoxotungstate anion.[111] In this case, hybridization leads to a significant positive shift in the redox potentials of the POM core, with the first reduction shifted by *ca.* 500 mV relative to the $\{P_2W_{17}\}$ parent anion, indicative of a substantial lowering of the LUMO energy in the hybrid complex. The photochemical properties were benchmarked against both $\{P_2W_{17}\}$ and $[P_2W_{18}O_{62}]^{6-}$ for the photo-oxidative decomposition of a model pollutant dye, where only the phosphonate-hybrid showed catalytic activity under visible irradiation (λ > 420 nm). Computational modelling supported these findings, showing that hybridization of the $\{P_2W_{17}\}$ cluster with the phosphonate moieties substantially alters the frontier orbital energies of the hybrid complex, resulting in an overall reduction in the energy of the HOMO-LUMO gap thanks to both the resonance and inductive effects exerted by the ligand groups. As an aside, it is also interesting to note that under strictly degassed conditions, the hybrid-complex could also effectively be fully photo-reduced by two electrons over 1 hour steady-state irradiation (λ > 390 nm) when employing DMF as both solvent and substrate/sacrificial reductant. This would suggest that it may have some potential as a multi-electron charge transfer catalyst in a manner similar to the examples reported by Proust *et al.* and Streb *et al.* above.

Further work in our group expanded on this orbital engineering approach by showing that the frontier orbital energies of the hybrid complex could be tuned by modifying the substituent at the para-position on the phenyl ring (Figure 11a, b).[108] Replacing the electron withdrawing 4-carboxyphenyl group with the less electron-withdrawing phenyl or 4-methoxyphenyl moieties, thus altering the overall inductive effect exerted on the POM, is shown to negatively shift the first redox potential – indicating destabilization of the LUMO level relative to the carboxylate-containing hybrid. This orbital engineering effect is also borne out by supporting DFT calculations which show a clear trend in the energies of the frontier orbitals, where stronger electron withdrawing groups lead to the greatest decrease in the energy of the HOMO-LUMO gap. Conversely, a fourth hybrid cluster in which the ligands are replaced by phosphonic acid groups – in which only inductive effects are present – shows an even more pronounced positive shift in the first reduction on the POM core (*ca.* +40 mV vs. the carboxylate-substituted hybrid). Evaluation of the photocatalytic properties of all four complexes reveals that the trends observed in the redox behaviour correlate strongly with the rate at which each hybrid photo-oxidizes indigo dye (Figure 11c), where a modest shift of 73 mV in the redox potential between the best (phosphonic acid) and worst (4-methoxyphenyl phosphonic acid) performing complexes corresponds to a tripling of the reaction rate under irradiation (λ > 420 nm). Generally speaking, the photo-oxidative performance of these hybrids is this comparable to recent reports of polyoxovanadate visible-light photocatalysts.[112-114]

Whilst the *vis-endo* photo-excitation of hybrid POM clusters is still very much a field in its infancy, it does present an interesting alternative to the more conventional *vis-exo* strategies pursued to date. Although there are clear limitations imposed by the need to excite into the LMCT band of the POM, which will almost certainly always require higher energy photoexcitation (i.e. λ < 450 nm) than organic or organometallic chromophores, the potential to meaningfully access the potent

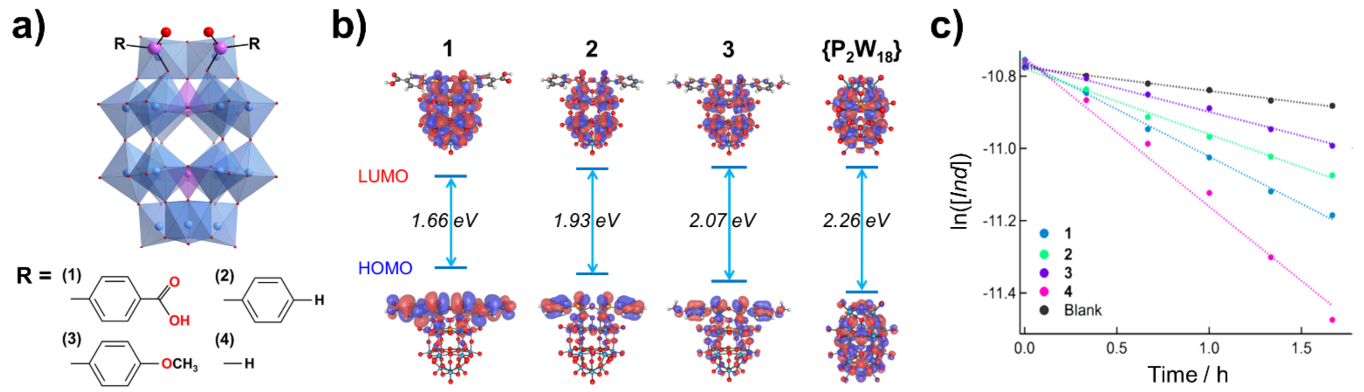


Figure 11: a) Schematic representation of the organophosphonate hybrid POMs reported by Newton, Oshio and co-workers, with organic substituents shown below; b) frontier orbital energies for the different hybrid species, showing the increasing HOMO-LUMO energy as the electron withdrawing capacity of the organic substituents is decreased (as compared to the parent anion, $[P_2W_{18}O_{62}]^{6-}$, and; c) comparative photocatalytic performance of the each hybrid towards oxidative decomposition of the model pollutant indigo dye, when irradiated (λ > 420 nm). Reprinted (adapted) with permission from ref. 108. Copyright 2017 American Chemical Society.

oxidative reactivity of the POM-centred photo-excited state (*via* the oxo-radical cation) under visible or solar irradiation is a significant advance and may open up a wealth of new applications. Furthermore, the relative simplicity of this approach stands in contrast with the more involved, multi-step ligand design strategies required for the state-of-the art hybrid complexes employed in *vis-exo* applications described above. In principle, hybridization of a suitable POM anion with *any* ligand group should modify the orbital properties of the POM (indeed, this is already indirectly observed in electrochemical studies of hybrid POMs where positive shifts in redox potential are a commonly accepted result of hybridization),[115] meaning that further optimization of this strategy (*i.e.* towards improved photochemical performance, product selectivity, *etc.*) should be achievable *via* judicious choice of ligand groups. Likewise, the freedom to design the hybrid complex without any need for additional chromophore species provides a relatively blank slate, paving the way for creative approaches involving surface functionalization, materials design and supramolecular assembly to explore new and novel photo- and/or photo-electro-chemical systems.

3. Conclusions and perspective

The focus of POM photochemistry has undergone a rapid change over the past decade or so, from the 'classic', *UV-endo* photo-oxidation chemistry described in Section 1.2, to predominantly the *vis-exo* based strategies targeting solar-driven energy storage and conversion. Whilst our focus in this *Perspective* is on hybrid-POMs, we acknowledge that transition-metal substituted POMs will continue to play a significant role in this field (as evidenced by the huge recent interest in TMSP water oxidation catalysts), particularly when combined with photosensitizers in class I hybrid assemblies (see Section 2.1 above). That said, covalent hybridisation strategies offer several key advantages, combining well-developed research on the synthesis and photo-physics of organic and organometallic chromophores (in addition to parallel research into their photo-catalytic reactivity), with the near-limitless molecular design possibilities presented by the growing field of hybrid-POM chemistry.

Regardless, several overarching challenges do however remain before widespread adoption of hybrid-POMs is a feasible concern in new photochemical technologies. These include both the cost and synthetic complexity of these clusters to manufacture and, more pressingly, their long-term stability. Whilst many POMs can be considered to be synthesised from relatively low-cost, earth-abundant elements, addressing their multi-step syntheses will require deeper study and greater adoption of new 'smart' synthetic technologies, such as the automated flow-syntheses pioneered by Cronin *et al.*[116, 117] Whilst the long-term stability of photo-active POM complexes remains challenging to both predict and engineer, emerging approaches combining active molecular species with surfaces or nano-porous materials have shown promise in stabilising a wide-variety of guests, and will offer an interesting avenue of further exploration in the context of POM-based photochemical (or photo-electrochemical) systems in the future.

Whilst future directions in the field are not necessarily easy to predict, we do believe that there are several key areas which will prove ripe for further exploration and should be well within reach over the following decade. These observations are summarised below, not as an authoritative guide, but rather as an optimistic outlook on the immediate future of the field:

i) The optimization of charge transfer properties, particularly towards facilitating efficient multi-electron reduction of the POM for solar-fuel applications, remains a key goal. Whilst the specific properties and electronic structure of the chromophore has already been shown to be of critical importance,[96] the vast majority of work thus far has been conducted on a handful of well-known POM archetypes (as discussed in Sections 2.1 and 2.2, above). Creative approaches which tune the electron acceptor properties of the POM itself (*i.e.* increasing its electron affinity) should therefore facilitate improved charge accumulation on the POM core. Furthermore, explicitly lowering the LUMO energy by modification of the POM has been shown in both the *vis-exo* and *vis-endo* approaches described above to lead to an improved photocatalytic reactivity (reductive H_2 evolution and organic oxidation, respectively).[97, 108]

ii) Given that POMs themselves appear to be relatively poor reduction catalysts, coupling the photo-induced charge accumulation behaviour of the POM with an appended catalytic centre may lead to a step-change in photocatalytic performance. As the synthesis of hybrid-POM species continues to improve, one strategy which could facilitate this photocatalytic approach would be the design and synthesis of photochemical triads to replace current state-of-the-art hybrid-dyads. For example, the combination of an appropriate sensitizer, charge accumulating POM centre and a tailored catalytic site (*e.g.* for H_2 evolution) could exploit sequential CT steps in a downhill electronic cascade, analogous to well-known biological electron transfer chains. Furthermore, such systems may also find application in photo-electrochemical systems where a sensitized POM dyad could be covalently coupled with *e.g.* an electrode surface. Whilst the preparation of such structurally complex hybrid-POMs on a preparative scale remains challenging, new synthetic breakthroughs should be expected to lead to more widespread exploration of three-component hybrid POM systems.

iii) As *vis-endo* approaches to POM photoactivation are very much in their infancy, there is significant scope to further optimize such systems. Whilst there are clear limitations on the ultimate effectiveness of the inductive ligand approach set-out in Section 2.3, this does not preclude modification of the POM core in order to tune the frontier orbital energies further. For instance, the polyoxovanadate systems reported by Zubieta, Schmitt and others,[118-123] may be readily amenable to this approach. Likewise, more fundamental modification of the POM core – such as by replacing oxygen atoms with sulfur – may lead to red-shifting of the absorption into the visible region. To date however, the photochemistry of these polyoxothiometalate species is largely unreported.[124, 125]

Another fundamental advantage of the *vis-endo* strategy is that is allows access to very high energy excited states centred on the POM itself, leading to a range of possible oxidation-, proton-coupled- and hydrogen-transfer reactivity which is not generally observed in *vis-exo* systems. Work in our group has already suggested that *vis-endo* excitation can lead to two electron reduction on the POM,[111] which may allow use of the POM itself as a photosensitizer in novel inorganic dyad systems.

iv) Lastly, whilst supramolecular design approaches are a common feature of hybrid-POM chemistry, they are relatively underexplored in a photochemical context. Such interactions can be used to generate new nanoscale supramolecular assemblies or engineer soft material properties. Recently our group has also shown that aggregation of hybrid-POM species into micellar structures can be used to reversibly modify their electronic properties,[48] whilst others have shown how hybrid-POMs can be readily combined with other functional nanostructured materials.[106] Host-guest interactions could play a key role in improving catalytic efficiency or selectivity, whilst opening new avenues in chiral catalysis or biochemical applications, to name but two. Indeed, the potential for functionalization of the POM with bio-compatible ligand groups coupled to, *e.g.* the generation of reactive oxygen species *via vis-endo* photo-excitation of the POM could lead to new applications in targeted photo dynamic therapies.[126]

In summary, this Perspective has presented an overview of the past, present and future directions in the visible-light driven photochemistry of organic-inorganic hybrid polyoxometalates and, specifically, those where the ligand component is covalently bound to the POM core (*i.e.* class II hybrids). It is our view that this field will continue to grow over the coming years as design, synthesis and characterisation approaches become ever more sophisticated and the POM community rises to meet the ongoing challenges in energy generation, conversion and storage presented by a globalised world.

Conflicts of interest

There are no conflicts to declare.

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