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# Hybrid Polyoxometalates: Keggin and Dawson Silyl Derivatives as Versatile Platforms

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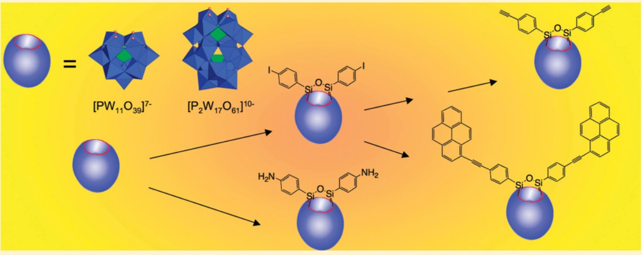
S *Supporting Information*

**ABSTRACT:** A new series of polyoxometalate-based hybrids has been synthesized. These covalently linked organic−inorganic materials represent valuable elementary building blocks ready for postfunctionalization, using classical organic reactions and couplings. This approach is exemplified by the grafting of an organic chromophore via a Sonogashira coupling.



## INTRODUCTION

Polyoxometalates (POMs) are discrete metal oxide clusters currently still receiving considerable attention because of their huge range of elemental compositions, sizes, and molecular structures.[1,2] Their structures are based upon $\{MO_p\}$ and $\{XO_q\}$ polyhedra sharing vertices, edges, or, more rarely, faces (M being an early transition metal in its highest oxidation state, mainly from groups 5 and 6, and X an heteroatom, like P, As, Si, ...) (Figure 1). They present good solubility and stability in aqueous and organic solvents (depending on the choice of the couterions) and, for some of them, reversible redox behavior. These properties have led to applications in many fields such as catalysis, medicine, and materials science.[3,4] Therefore POMs have been widely used for the preparation of hybrid materials and functional devices.[5,6] Covalent POM-based hybrids are much less developed than hybrids in which the POM and the organic component are linked through noncovalent interactions, e.g. van der Waals contacts, hydrogen bondings, and/or ionic interactions. Nevertheless, the covalent approach offers several advantages, in particular it should enhance the directionality and the interaction between the inorganic and organic components.[5,7,8] As a matter of fact, we thought that it would be of great interest to develop synthetic tools adapting classical reactions from organic synthesis to POM derivatization. We focused our attention on the synthesis of organo-silyl derivatives of the redox active Keggin and Dawson heteropolytungstates (i.e., derived from the $[PW_{12}O_{40}]^{3-}$ and $[P_2W_{18}O_{62}]^{6-}$ POMs, respectively, Figure 1), since the resulting multifunctionalized hybrids exhibit substantial hydrolytic and thermal resistance. Following some preliminary studies reporting the synthesis of a Keggin-type POM-based organic/inorganic platform bearing a iodo aryl function,[9] we decided to extend our work to the Dawson series and to other organic moieties that could be involved in classical coupling reactions.

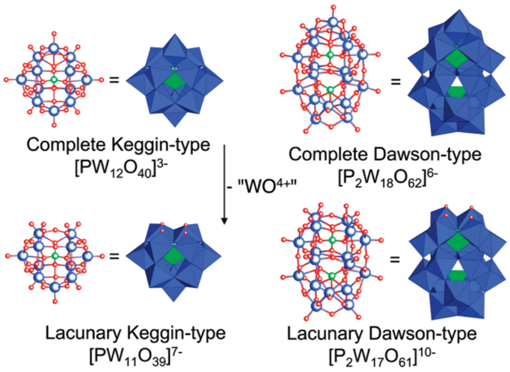


**Figure 1.** Complete and lacunary Keggin-type (left) and Dawson-type (right) POM structures in ball-and-stick and polyhedral representations. In the polyhedral representation, the $MO_6$ octahedra are depicted, with oxygen atoms at the vertices and metal cations buried inside. These molecular oxide structures are often more readily discerned in polyhedral representation than in ball-and-stick representation. Color code: $MO_6$ octahedra, blue; $PO_4$ tetrahedra, green.

To perform covalent postfunctionalization of POMs, appropriate pendant organic functions need to be grafted on the polyanion. Among them, iodo aryl, terminal alkyne, and amino aryl groups appear to be promising candidates, and, in some cases, have already been used for postfunctionalization of POMs.[9−17] Iodo aryl groups can be involved in palladium-catalyzed

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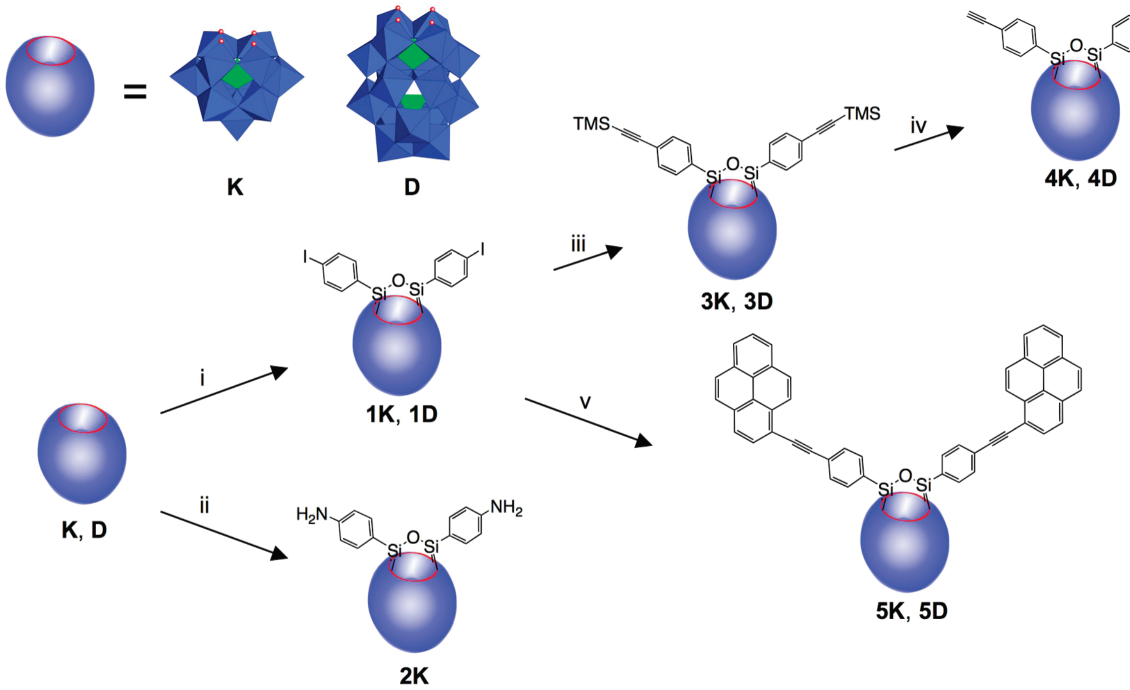

**Figure 2.** Synthetic routes to the organo-silyl POM-based hybrids from $[PW_{11}O_{39}]^{7-}$ (K) and $[P_2W_{17}O_{61}]^{10-}$ (D): (i) $(EtO)_3SiPhI$, HCl; (ii) $(MeO)_3SiPhNH_2$, HCl; (iii) $Pd(PPh_3)_2Cl_2$, CuI, TEA, trimethylsilylacetylene; (iv) $AgNO_3$; (v) $Pd(PPh_3)_2Cl_2$, CuI, TEA, 1-ethynylpyrene.

C−C coupling reactions.[10,18] In particular, Sonogashira couplings are attractive since they allow the grafting of organic moieties with a controlled directionality under mild conditions. Such an approach has been already employed with success by others[11−13] and us[9] to graft organic tethers on POMs. Amino groups and anilines react with carboxylic acid derivatives to form an amide link.[14,19,20] Aniline can also be transformed to diazonium precursors (diazotation reaction) for grafting onto surfaces.[13] Finally terminal alkynes can be involved in Sonogashira and Huisgen couplings.[15,16] Besides, we have reported POM-based hybrids functionalized with a terminal alkyne for anodic electrografting to silicon wafer.[17]

We thus herein describe the synthesis of organic−inorganic POM-based hybrids displaying the organic functionalities mentioned above. These compounds have been synthesized both in the Keggin and Dawson series. In one case, the coupling to an organic photoactive antenna was performed to validate our approach.

## ■ RESULTS AND DISCUSSION

**Synthesis of POM-Based Hybrid Platforms Bearing Iodo Aryl and Amino Aryl Functions.** Complete POMs are usually hard to process since terminal, i.e. multiply bonded, oxo ligands are rather weak nucleophiles. However, lacunary species, missing formally one (or several) octahedron(dra), react with a large variety of transition metals and electrophilic organic or organometallic groups. $K_7[PW_{11}O_{39}]\cdot 14H_2O$ and $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ were used in this study since they offer a similar oxo environment in their lacuna. These lacunary species still differ by their charge, shape, and electronic properties. We recently described the synthesis of the POM-based hybrid **1K** as a tetrabutylammonium (TBA) salt (denoted **TBA-1K**).[9] This reaction was adapted with success to the synthesis of the Dawson-type analogue **TBA-1D** and the synthesis of the hybrid **TBA-2K** bearing two aniline groups (Figure 2). The reaction between the lacunary POM and the relevant organosilane is performed in an acetonitrile/water mixture in which the apparent pH of the solution is fixed at 2. An excess of the trialkoxysilane is required to improve the purity of the resulting hybrid, but we found no improvement if more than 4 equiv were used. Also we lately found that lowering the temperature to −20 °C was also useful to increase the purity of the crude product.

**From Iodo Aryl to Terminal Alkyne Platforms.** The trimethylsilyl-protected alkyne hybrids **TBA-3K** and **TBA-3D** can easily be synthesized from **TBA-1K** and **TBA-1D**, respectively, through a Sonogashira coupling.[9] This reaction is very efficient since it is completed in 4 to 6 min under very mild microwave activation (50 °C). The dark blue coloration of the solution suggested a reduction of the POM probably catalyzed by the Pd(0) catalyst. After completion of the reaction, one equivalent of tetrabutylammonium perbromide ($TBABr_3$) was thus added to the solution, which instantly turned orange/yellow, witnessing the reversible POM reoxidation. For the synthesis of the Keggin-type hybrid **TBA-3K**, addition of an excess of TBABr to the solution allows for the recovery of **3K** as a tetrabutylammonium salt through its precipitation by further addition of ethanol. Nevertheless, for the synthesis of **TBA-3D**, the previous procedure yielded the POM as a mixture of triethylammonium and tetrabutylammonium salt. The crude was thus redissolved in dichloromethane in the presence of an excess of TBABr and washed three times with water to eliminate the last traces of triethylammonium.

To synthesize the hybrid bearing terminal alkyne moieties classical cleavage reactions (i.e., fluoride or base)[21] could not be adapted, since they result in the partial cleavage of the organosilyl tether to the POM. Nevertheless, we found that addition of $AgNO_3$[21−23] selectively leads to the protiodesylation of the

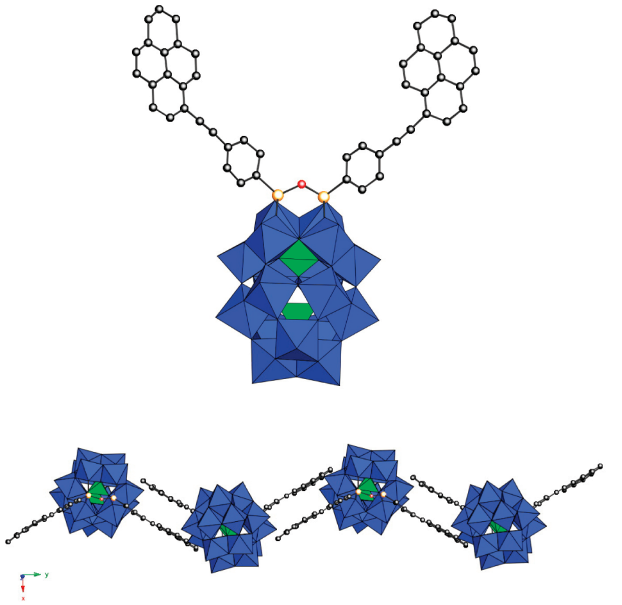

**Figure 3.** Top: Crystal structure (combined polyhedral/ball-and-stick representation) of polyanion **5D**. Bottom: Packing in the crystal lattice. Solvent molecules and counterions have been omitted for clarity. $WO_6$ and $PO_4$ polyhedra are shown in blue and green, respectively. The Si, O, and C atoms are shown in yellow, red, and black, respectively.

trimethylsilyl-alkyne group. A large excess of silver salt is necessary to initiate the reaction, possibly due to strong interactions between Ag(I) cations and POM anions. A careful extraction of the silver salts, by precipitation of AgBr by addition of TBABr, is needed since silver(I) is known to interact with the terminal oxo ligands of the POM,[24] especially in the solid state.

**Purification of the Hybrids.** The reactivity of Keggin ($[PW_{11}O_{39}]^{7-}$) and Dawson lacunary POMs ($[P_2W_{17}O_{61}]^{10-}$) is similar. Nevertheless, by extending our work to the Dawson series the purification methods had to be adapted since Keggin and Dawson heteropolyanions present different charge, solubility, and counterion affinity (see also above the different workup for **TBA-3K** and **TBA-3D**).

Separation techniques classically used in organic chemistry (silica and alumina gel chromatographies) cannot be adapted for the purification of POM-based hybrids since they result in their adsorption or degradation. As a consequence, all the reactions performed on POMs have to be straightforward and quantitative since mixtures of POM-based hybrids are hardly separable. Usually, separations of POMs are performed by a series of crystallization−filtration steps. Unfortunately, this technique requires the formation of crystals, which are often difficult to get from tetrabutylammonium salts. Nevertheless, selective precipitations by addition of minimum amounts of ethanol on a solution of the hybrid in an organic solvent ($CH_2Cl_2$, MeCN, DMF, ...) often help to get microanalysis purity of the desired compound. Finally, the exclusion size chromatography with a Sephadex LH20 column, using dichloromethane or acetonitrile as eluting solvent, can also purify the POM-based hybrids from organic impurities.

**Covalent Grafting of an Organic Chromophore.** POMs are attractive candidates for the development of photochemical devices aiming at photocumulative electron transfers. However, the attachment of a light-harvesting antenna is advisible, since POMs themselves are only photoactive in the UV part of the solar spectrum. Pyrene is a good candidate as it is easily functionalized and presents a strong absorption and luminescence in the visible region. 1-ethynylpyrene was synthesized in two steps from 1-bromopyrene.[25] The covalent attachments of 1-ethynylpyrene to **1K** and **1D** platforms are performed in dimethylformamide, under microwave irradiation for 40 min with a set temperature of 70 °C. For microanalysis purpose, a purification by selective precipitations of the crude in DMSO/$CH_2Cl_2$/EtOH mixture gives **TBA-5K** and **TBA-5D** in moderate to good yields (58% and 94%, respectively). The photophysical properties of hybrids **TBA-5K** and **TBA-5D** will be described elsewhere.

Single crystals were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **TBA-5D** (Figure 3). Compound **TBA-5D** crystallizes in the orthorhombic system with the $P2_12_12_1$ space group. The asymmetric unit contains one hybrid POM in general position and 6 TBA cations, located through successive difference electron density maps, in agreement with the elemental analysis. The Si atoms display a tetrahedral environment and each silyl group is linked to two different terminal oxygen atoms of the lacunary POM site. The lengths of the Si−O bonds are in the range 1.58−1.66(2) Å while the W−O bond lengths in the lacunary site are in the range 1.88−1.97(2) Å. These values are close to those reported for $[\alpha_2\text{-}P_2W_{17}O_{61}\{O(SiPh)_2\}]^{6-}$.[26] The Si−C bond lengths, in the range 1.92−1.97(3) Å, are slightly higher than those reported for $[\alpha_2\text{-}P_2W_{17}O_{61}\{O(SiPh)_2\}]^{6-}$ (1.85(1) Å). Finally, The Si−O−Si bond angle of 124.6(14)°, similar to the 127.4(7)° for $[\alpha_2\text{-}P_2W_{17}O_{61}\{O(SiPh)_2\}]^{6-}$, is not very sensitive to the substituent on the silicon, as expected. In the crystal lattice, each pyrene unit shows $\pi$-stacking interactions with an aryl ring of a neighboring complex, with a separation distance of about 3.4 Å.

Both **TBA-5K** and **TBA-5D** hybrids display similar $^1H$ NMR profile (Figure 4). In DMSO-$d_6$ the $^1H$ resonances of the pyrene moieties are located in the 8−9 ppm region while the $^1H$ resonances of the silyl-aryl moieties are located in the 7.5−8 ppm region. In the case of **TBA-5K** these last two resonances accidentally overlap and show a very pronounced roof effect.

Cyclic voltammetry studies of **TBA-5K** and **TBA-5D** (Figure 5) were carried out in DMF at a glassy carbon electrod, with $TBAPF_6$ as the supporting electrolyte, a saturated calomel electrode (SCE), and ferrocene as internal reference. In the reduction part, **TBA-5K** displays four reversible reduction processes. The first three waves at $E_{1/2} = -0.38$, $-0.97$, and $-1.70$ V vs SCE correspond to monoelectronic processes located at the tungstic framework, while the last reversible redox process at $E_{1/2} = -1.75$ V vs SCE is attributed to the reduction of both pyrene units, by comparison with free pyrene. In compound **TBA-5D**, the reduction of both pyrenes appears at the same potential as the third monoelectronic reduction of the POM at $-1.75$ V vs SCE, the first two redox processes being observed at $E_{1/2} = -0.73$ and $-1.14$ V vs SCE. In the oxidative part, **TBA-5K** and **TBA-5D** both display an irreversible process around 1.3 V vs SCE, attributed to the oxidation of the pyrene units.

## CONCLUSION

We describe herein the synthesis of a set of inorganic/organic POM-based hybrids, in which the organic moieties are covalently connected to the inorganic POM framework. We first extended our preliminary work from the Keggin to the Dawson series.

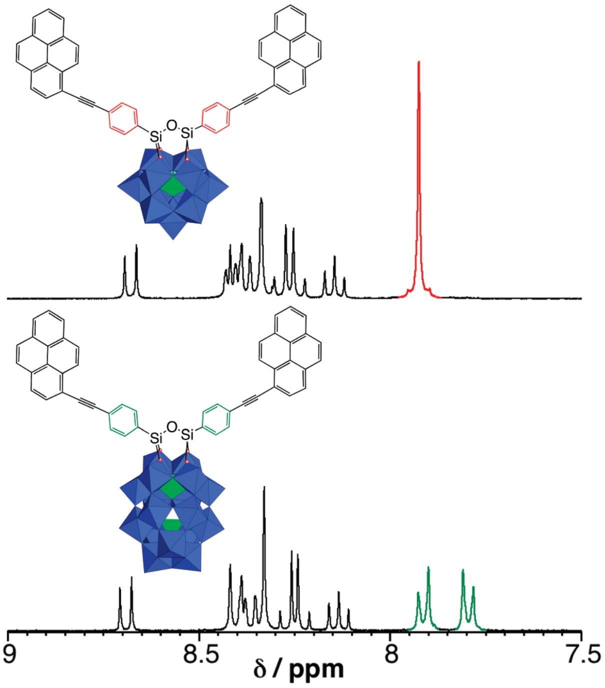

**Figure 4.** Enlargement of the 7.5−9.0 ppm region of the $^1$H NMR (DMSO-$d_6$, 300 MHz) spectrum of **TBA-5K** (top) and **TBA-5D** (down).

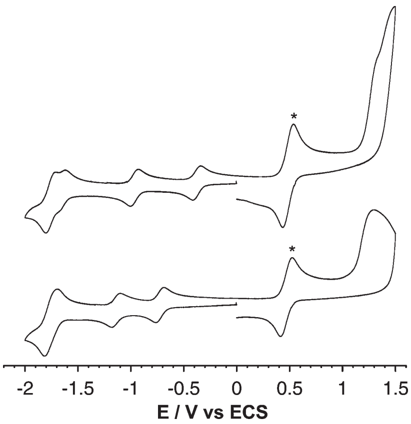

**Figure 5.** Cyclic voltammogram of a $10^{-3}$ M solution of **TBA-5K** (top) and **TBA-5D** (down) in DMF containing 0.1 M TBAPF$_6$ and $10^{-3}$ M ferrocene (internal reference): scan rate, 200 mV s$^{-1}$; working electrode, glassy carbon; reference electrode, SCE. The peaks noted with an asterisk correspond to the oxidation of the ferrocene.

Even though the reactivity of the parent lacunary POMs ($[PW_{11}O_{39}]^{7-}$ and $[P_2W_{17}O_{61}]^{10-}$) is similar, the purification methods had to be adapted since Keggin and Dawson heteropolyanions present different charge, solubility, and counterion affinity. The extension of our hybrids to the Dawson series widens the electronic tunability of our system since Keggin and Dawson complexes display different redox behavior. We also synthesized two new POM-based hybrid platforms bearing terminal alkyne or amino aryl moieties. These platforms are potentially postfunctionalizable and offer the possibility to address a large range of building blocks. By way of postfunctionalization of these hybrids, two pyrene-derivatized POMs were synthesized and characterized. These compounds are new examples of hybrids in which the POMs is covalently linked to chromophores. Such compounds will be studied as artificial photosynthetic models. We will also test their implementation in photovoltaic devices.

## ■ EXPERIMENTAL SECTION

**Synthesis of $(TBA)_6[P_2W_{17}O_{62}\{O(Si\text{-}PhI)_2\}]$ (TBA-1D).** $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ (2 g, 0.407 mmol, 1 equiv) was set in suspension in a 30 mL mixture of acetonitrile/water (2/1). The apparent pH of the suspension was fixed at 2 by dropwise addition of 1 M hydrochloric acid at 0 °C. 1-Iodo-4-(triethoxysilyl)benzene (600 mg, 1.628 mmol, 4 equiv) was added at −20 °C. After being stirred for 2 h at this temperature the solution was stirred at room temperature under air atmosphere overnight. TBABr (920 mg, 2.86 mmol, 7 equiv) was then added to precipitate the polyoxometalate as a tetrabutylammonium salt. After partial evaporation of the acetonitrile, the crude solid was recovered by centrifugation. For purification purposes, the compound was dissolved in acetonitrile and ethanol was then added in similar volume to initiate precipitation. After removal of the precipitate by filtration, the filtrate was precipitated by further addition of Et$_2$O. The obtained solid was finally dissolved in dichloromethane and filtered on a small column of Sephadex LH20, using dichloromethane as eluant. After evaporation of the solvent **TBA-1D** was obtained as a white powder. Yield: 90%. $^1$H NMR (CD$_3$CN): $\delta$ 7.76 (d, $J$ = 8.1 Hz, 4H), 7.58 (d, $J$ = 8.1 Hz, 4H), 3.15 (m, 48H), 1.64 (m, 48H), 1.41 (sextuplet, 7.2 Hz, 48H), 0.99 (t, $J$ = 7.2 Hz, 72H). $^{31}$P NMR (CD$_3$CN): $\delta$ −9.22 and −12.19 ppm. MS (ESI): most intense peaks, $\{\text{aggregates}\}^{x-}$ $m/z$ (%): $\{H[\mathbf{1D}]\}^{5-}$ 928.5 (64), calcd 928.1; $\{TBA[\mathbf{1D}]\}^{5-}$ 976.8 (100), calcd 976.6; $\{H,TBA[\mathbf{1D}]\}^{4-}$ 1220.4 (4), calcd 1221.2; $\{TBA_2[\mathbf{1D}]\}^{4-}$ 1281.6 (11), calcd 1281.8; IR (KBr, cm$^{-1}$): $\nu$ 2962 (s), 2935 (s), 2874 (s), 1570 (m), 1483 (s), 1378 (m), 1151 (m), 1124 (s), 1089 (s), 1042 (s), 988 (m), 955 (s), 916 (s), 813 (s), 767 (s), 722 (sh), 598 (m), 562 (m), 529 (s), 389 (s), 353 (s), 330 (s). Calcd elemental analysis for $P_2W_{17}O_{62}Si_2I_2C_{108}H_{224}N_6$ (%): C 21.28, H 3.70, N 1.38. Found: C 21.17, H 3.67, N 1.38.

**Synthesis of $(TBA)_3[PW_{11}O_{39}\{O(Si\text{-}PhNH_2)_2\}]$ (TBA-2K).** $K_7[PW_{11}O_{39}]\cdot 14H_2O$ (1.0 g, 0.312 mmol, 1 equiv) was set in suspension in an acetonitrile/water mixture (35/15 mL) at 0 °C. *p*-Aminophenyltrimethoxysilane (400 mg, 1.87 mmol, 6 equiv) dissolved in 10 mL of CH$_3$CN was added to the solution. The apparent pH of the suspension was fixed at 2.3 by dropwise addition of 1 M hydrochloric acid at 0 °C. The obtained solution was stirred at room temperature overnight. The solution was then filtrated and TBABr (0.503 g, 1.56 mmol, 5 equiv) was added to the filtrate to precipitate the polyoxometalate. After evaporation of the acetonitrile under reduced pressure, the resulting solid was separated from the aqueous layer by centrifugation. The compound was triturated with ethanol, filtrated, and washed with diethyl ether to obtain **2K** as a mixed acidic/tetrabutylammonium salt (ca. 0.3 H$^+$ for 2.7 TBA$^+$). To fully deprotonate the aniline moieties the solid was redissolved in a minimum of acetonitrile and added to an acetonitrile solution containing triethylamine (35 $\mu$L, 0.250 mmol, 0.8 equiv) and a large excess of TBABr. The polyoxometalate was finally precipitated with EtOH and washed with diethyl ether to obtain **TBA-2K** as a brownish solid. Yield: 74%. $^1$H NMR (CD$_3$CN): $\delta$ 7.54 (d, $J$ = 8.4 Hz, 4H), 6.73 (d, $J$ = 8.4 Hz, 4H), 4.41 (s, 4H), 3.15 (m, 24H), 1.62 (m, 24H), 1.38 (sextuplet, 7.2 Hz, 24H), 0.99 (t, $J$ = 7.2 Hz, 36H); $^{31}$P NMR (CD$_3$CN): $\delta$ −12.06 ppm; MS (ESI): most intense peaks, $\{\text{aggregates}\}^{x-}$ $m/z$ (%): $\{[\mathbf{2K}]\}^{3-}$ 977.9 (100), calcd 978.1; $\{TBA[\mathbf{2K}]\}^{2-}$ 1588.9 (3), calcd 1587.8; IR (KBr, cm$^{-1}$) $\nu$ 2962 (s), 2933 (s), 2874 (s), 1599 (m), 1508 (m), 1482 (m), 1380 (m), 1131 (m), 1111(s), 1067 (s), 1036 (s), 964 (s), 869 (s), 819 (s), 707 (sh), 671 (sh), 595 (m), 516 (s), 392 (s). Calcd elemental analysis for $PW_{11}O_{40}Si_2C_{60}H_{120}N_5$ (%): C 19.68, H 3.30, N 1.91. Found: C 19.48, H 3.25, N 1.79.

**Synthesis of $(TBA)_6[P_2W_{17}O_{61}\{O(Si\text{-}Ph\text{-}ethynyl\text{-}TMS)_2\}]$ (TBA-3D).** A mixture of **TBA-1D** (1 g, 0.164 mmol, 1 equiv), $[Pd(PPh_3)_2Cl_2]$ (0.013 mmol, 8 mol %), and CuI (0.025 mmol, 15 mol %) was prepared in 35 mL of freshly distilled acetonitrile. After careful degassing with argon during 10 min, trimethylsilylacetylene (0.5 mmol, 3 equiv) and freshly distilled $Et_3N$ (1.64 mmol, 10 equiv) were added. The mixture was stirred at 50 °C for 6 min under microwave irradiation to give a blue solution indicating the reduction of the polyoxometalate. $TBABr_3$ (0.164 mmol, 1 equiv) and TBABr (3.28 mmol, 20 equiv) were then added successively under argon, respectively, to oxidize the polyoxometalate and to favor its recovery as a tetrabutylammonium salt rather than a mixed tetrabutylammonium/triethylammonium salt. The solvent was evaporated and the resulting crude washed with ethanol. The solid was then dissolved in dichloromethane and 1 g of TBABr was added. The solution was washed 3 times with water to eliminate the last traces of triethylammonium bromide. The solvent was evaporated and the residue washed with EtOH and $Et_2O$ to obtain **TBA-3D** as a light brownish powder. Yield: 81%. $^1H$ NMR ($CD_3CN$): $\delta$ 7.80 (d, $J$ = 8.1 Hz, 4H), 7.43 (d, $J$ = 8.1 Hz, 4H), 3.15 (m, 48H), 1.64 (m, 48H), 1.41 (sextuplet, 7.2 Hz, 48H), 0.99 (t, $J$ = 7.2 Hz, 72H), 0.24 (s, 18H). $^{31}P$ NMR ($CD_3CN$): $\delta$ −9.20 and −12.18 ppm. MS (ESI): most intense peaks, $\{aggregates\}^{x-}$ $m/z$ (%): $\{H[\mathbf{3D}]\}^{5-}$ 916.7 (100), calcd 916.6; $\{TBA[\mathbf{3D}]\}^{5-}$ 965.1 (88), calcd 965.0; $\{H,TBA[\mathbf{3D}]\}^{4-}$ 1206.1 (4), calcd 1206.8; $\{TBA_2[\mathbf{3D}]\}^{4-}$ 1266.5 (7), calcd 1266.4. IR (KBr, $cm^{-1}$): $\nu$ 2962 (s), 2935 (s), 2874 (s), 2156 (w), 1637 (m), 1483 (s), 1380 (m), 1250 (m), 1118 (s), 1089 (s), 1041 (s), 988 (m), 955 (s), 916 (s), 813 (s), 766 (s), 624 (m), 597 (m), 549 (m), 520 (s), 389 (s), 350 (m), 329 (s). Calcd elemental analysis for $P_2W_{17}O_{62}Si_4C_{118}H_{242}N_6$ (%): C 23.48, H 4.04, N 1.39. Found: C 23.48, H 3.88, N 1.30.

**Synthesis of $(TBA)_3[PW_{11}O_{39}\{O(Si\text{-}Ph\text{-}acetylene)_2\}]$ (TBA-4K).** A solution of **TBA-3K** (200 mg, 0.052 mmol, 1 equiv) in a 20 mL mixture of acetonitrile/methanol/$H_2O$ in a 7/2/1 ratio was prepared. $AgNO_3$ (44 mg, 0.26 mmol, 5 equiv) was then added, and the resulting mixture was stirred in the dark at room temperature for 2 days. TBABr (20 equiv) was added and after filtration of AgBr the filtrate was partially concentrated and **TBA-4K** precipitated by addition of ethanol and filtered. The solid was finally washed with ethanol and dried with diethyl ether to get **TBA-4K** (140 mg) as a white powder. Yield: 74%. $^1H$ NMR ($CD_3CN$): $\delta$ 7.82 (d, $J$ = 8.1 Hz, 4H), 7.58 (d, $J$ = 8.1 Hz, 4H), 3.47 (s, 2H), 3.10 (m, 24H), 1.62 (m, 24H), 1.37 (sextuplet, $J$ = 7.2 Hz, 24H), 0.98 (t, $J$ = 7.2 Hz, 36H). $^{31}P$ NMR ($CD_3CN$): $\delta$ −11.89 ppm. MS (ESI): most intense peaks, $\{aggregates\}^{x-}$ $m/z$ (%): $\{[\mathbf{4K}]\}^{3-}$ 984.0 (100), calcd 983.4; $\{TBA[\mathbf{4K}]\}^{2-}$ 1597.2 (10), calcd 1597.3. IR (KBr, $cm^{-1}$): $\nu$ 2964 (s), 2936 (s), 2875 (s), 2108 (vw), 1483 (s), 1470 (s), 1382 (m), 1110 (s), 1066 (s), 1040 (s), 1019 (w), 996 (sh), 983 (sh), 965(s), 872 (s), 824 (s), 770 (sh), 718 (sh), 630 (m), 595 (m), 520 (s), 393 (s), 351 (m). Calcd elemental analysis for $PW_{11}O_{40}Si_2C_{64}H_{118}N_3$ (%): C 20.89, H 3.23, N 1.14. Found: C 20.69, H 3.31, N 1.36.

**Synthesis of $(TBA)_6[P_2W_{17}O_{61}\{O(Si\text{-}Ph\text{-}acetylene)_2\}]$ (TBA-4D).** Starting from **TBA-3D** (200 mg, 0.033 mmol, 1 equiv) the same procedure as for **TBA-4K** was followed, using 10 equiv of $AgNO_3$. **TBA-4D** was obtained as a white solid. Yield: 56%. A slight excess of TBABr is observed in the $^1H$ NMR spectrum and confirmed by elemental analysis. $^1H$ NMR ($CD_3CN$): $\delta$ 7.81 (d, $J$ = 8.1 Hz, 4H), 7.49 (d, $J$ = 8.4 Hz, 4H), 3.39 (s, 2H), 3,14 (m, 52H), 1.65 (m, 52H), 1.41 (sextuplet, 7.2 Hz, 52H), 0.98 (t, $J$ = 7.2 Hz, 78H). $^{31}P$ NMR ($CD_3CN$): $\delta$ −9.21 and 12.18 ppm. MS (ESI): most intense peaks, $\{aggregates\}^{x-}$ $m/z$ (%): $\{H[\mathbf{4D}]\}^{5-}$ 887.7 (90), calcd 887.8; $\{TBA[\mathbf{4D}]\}^{5-}$ 936.4 (100), calcd 936.0; $\{H,TBA[\mathbf{4D}]\}^{4-}$ 1170.4 (2), calcd 1170.5; $\{TBA_2[\mathbf{4D}]\}^{4-}$ 1230.1 (10), calcd 1230.1. IR (KBr, $cm^{-1}$): $\nu$ 2962 (s), 2935 (s), 2873 (s), 2106 (vw), 1484 (s), 1381 (m), 1117 (s), 1089 (s), 1041 (s), 1019 (w), 988 (sh), 955 (s), 916 (s), 812 (s), 766 (sh), 622 (w), 595 (w), 529 (m), 392 (m), 347 (m). Calcd elemental analysis for $P_2W_{17}Si_2O_{62}C_{112}H_{226}N_6\cdot(NBu_4Br)_{0.5}$ (%): C 23.81, H 4.06, N 1.50. Found: C 24.10, H 4.03, N 1.48.

**Synthesis of $(TBA)_3[PW_{11}O_{39}\{O(Si\text{-}Ph\text{-}ethynylpyrene)_2\}]$ (TBA-5K).** A mixture of **TBA-1K** (191 mg, 0.05 mmol, 1 equiv), 1-ethynylpyrene (28 mg, 0.125 mmol, 2.5 equiv), $[Pd(PPh_3)_2Cl_2]$ (0.005 mmol, 10 mol %), and CuI (0.0075 mmol, 15 mol %) in 5 mL of dried and freshly distilled DMF was prepared. After careful degassing with argon for 10 min, freshly distilled $Et_3N$ (0.5 mmol, 10 equiv) was added. The mixture was stirred at 70 °C for 45 min under microwave irradiation. After cooling to room temperature $TBABr_3$ (24 mg, 0.05 mmol, 1 equiv) was added to the mixture under argon. After the addition of TBABr (20 equiv) the polyoxometalate was precipitated with $Et_2O$. The obtained solid was finally dissolved in a solution of DMSO and $CH_2Cl_2$ (1/1) and precipitated with EtOH to obtain **TBA-5K** as a brownish solid. Yield: 58%. $^1H$ NMR (DMSO-$d_6$): $\delta$ 8.68 (d, $J$ = 9.1, 2H), 8.31−8.43 (m, 10H), 8.28 (d, $J$ = 9.0 Hz, 2H), 8.23 (d, $J$ = 9.0 Hz, 2H), 8.14 (t, $J$ = 7.7 Hz, 2H), 7.90 (m, 8H), 3.16 (m, 24H), 1.57 (m, 24H), 1.31 (sextuplet, 7.2 Hz, 24H), 0.93 (t, $J$ = 7.2 Hz, 36H). $^{31}P$ NMR (DMSO-$d_6$): $\delta$ −12.05 ppm. MS (ESI): most intense peaks, $\{aggregates\}^{x-}$ $m/z$ (%): $\{[\mathbf{5K}]\}^{3-}$ 1117.8 (100), calcd 1117.1; $\{TBA[\mathbf{5K}]\}^{2-}$ 1796.6 (3), calcd 1797.8. IR (KBr, $cm^{-1}$): $\nu$ 2962 (s), 2935 (s), 2874 (s), 2205 (vw), 1594 (w), 1481 (m), 1380 (m), 1111 (s), 1067 (s), 1039 (s), 1017 (w), 996 (sh), 983 (sh), 965 (s), 872 (s), 823 (s), 767 (s), 717 (m), 689 (w), 586 (w), 522 (m), 395 (m). Calcd elemental analysis for $PW_{11}O_{40}Si_2C_{96}H_{134}N_3$ (%): C 28.26, H 3.31, N 1.03. Found: C 28.52, H 3.33, N 1.08.

**Synthesis of $(TBA)_6[P_2W_{17}O_{61}\{O(Si\text{-}Ph\text{-}ethynylpyrene)_2\}]$ (TBA-5D).** A mixture of **TBA-1D** (300 mg, 0.05 mmol, 1 equiv), 1-ethynylpyrene (28 mg, 0.125 mmol, 2.5 equiv), $Pd(PPh_3)_2Cl_2$ (0.005 mmol, 10 mol %), and CuI (0.0075 mmol, 15 mol %) in 5 mL of dried and freshly distilled DMF was prepared. After careful degassing with argon for 10 min, freshly distilled $Et_3N$ (1 mmol, 20 equiv) was added. The mixture was stirred at 70 °C for 40 min under microwave irradiation. After cooling to room temperature $TBABr_3$ (24 mg, 0.05 mmol, 1 equiv) and TBABr (20 equiv) in 30 mL of $CH_2Cl_2$ were added to the mixture under argon. The solution was washed 4 times with water and precipitated with diethyl ether. The obtained solid was finally dissolved in DMSO and precipitated with EtOH to obtain **TBA-5D** as a clear yellow/brown solid. Yield: 94%. $^1H$ NMR (DMSO-$d_6$): $\delta$ 8.69 (d, $J$ = 9.1 Hz, 2H), 8.33−8.42 (m, 10H), 8.27 (d, $J$ = 9.0 Hz, 2H), 8.23 (d, $J$ = 9.0 Hz, 2H), 8.13 (t, $J$ = 7.7 Hz, 2H), 7.91 (d, $J$ = 8.1 Hz, 4H), 7.80 (d, $J$ = 8.1 Hz, 4H), 3.16 (m, 48H), 1.57 (m, 48H), 1.33 (sextuplet, 7.2 Hz, 48H), 0.93 (t, $J$ = 7.2 Hz, 72H). $^{31}P$ NMR (DMSO-$d_6$): $\delta$ −9.31 and −12.32 ppm. MS (ESI): most intense peaks, $\{aggregates\}^{x-}$ $m/z$ (%): $\{H[\mathbf{5D}]\}^{5-}$ 968.2 (80), calcd 968.0; $\{TBA[\mathbf{5D}]\}^{5-}$ 1016.2 (100), calcd 1015.6; $\{H,TBA[\mathbf{5D}]\}^{4-}$ 1270.0 (6), calcd 1270.0; $\{TBA_2[\mathbf{5D}]\}^{4-}$ 1331.0 (10), calcd 1330.6. IR (KBr, $cm^{-1}$): $\nu$ 2961 (s), 2933 (s), 2873 (s), 2205 (vw), 1600 (w), 1483 (m), 1380 (m), 1150 (w), 1119 (s), 1089 (s), 1041 (s), 1018 (w), 988 (sh), 954 (s), 916 (s), 812 (s), 765 (s), 720 (sh), 688 (w), 581 (w), 528 (m), 391 (m). Calcd elemental analysis for $P_2W_{17}O_{62}Si_2C_{144}H_{242}N_6$ (%): C 27.48, H 3.88, N 1.34. Found: C 27.24, H 3.75, N 1.34.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** General methods, details of the X-ray crystal structure determination, and crystallographic data in CIF format of compound **TBA-5D**, $^1H$ and $^{31}P$ NMR spectra of all reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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