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Postfunctionalization of Keggin silicotungstates by general coupling procedures

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ABSTRACT

Tetrabutyl ammonium (TBA) salts of organotin derivatives of polyoxometalates $(TBA)_5[SiW_{11}O_{39}\{Sn(CH_2)_2COOH\}]$ (**1**), $(TBA)_4[SiW_{11}O_{39}\{Sn(CH_2)_2CO\}]$ (**2**), $(TBA)_5[SiW_{11}O_{39}\{Sn(CH_2)_2CONH(CH_2)_3N_3\}]$ (**3**), $TBA_5[SiW_{11}O_{39}\{Sn(CH_2)_2CONH(CH_2)_3(N_3C_2H)C_{10}H_9Fe\}]$ (**4**) and an ammonium salt $(NH_4)_5[SiW_{11}O_{39}\{Sn(CH_2)_2CONH(CH_2)_3N_3\}]$(**3′**) have been synthesized for the first time by adapting the organic functionalization strategies developed earlier for phosphotungstates. The products were characterized using FTIR, NMR, ESI MS, and electrochemical techniques. The Keggin silicotungstate is more nucleophilic than the Keggin phosphotungstate and displays reactivity previously known only for Dawson phosphotungstates. The methodology of CuAAC "click" reaction for silico- and phosphotungstates allows the coupling by a common protocol of diverse POMs with different redox properties, which is potentially useful for bioelectroanalytical applications with redox labels.

1. Introduction

Polyoxometalates (POM) are structurally well defined anionic metal oxygen clusters that exhibit great diversity in nuclearity, size, shape and electrochemical properties [1–6]. They are constructed from early transition metals M (mainly W, Mo or V) and oxygen, and often with a heteroatom (Si, P, Ge, etc). Although such compounds have been known for a very long time, their fascinating properties of high added value (tunable redox properties, large size, high negative charges, photo and electrochromism [2], magnetism [3,7,8]) and potential applications in various fields including catalysis [9] medicine [2,4,10–12] as well as material science [3,6] are the driving forces for the increasing attention they have garnered in the past decades.

Organic functionalization of POMs occurs via either replacement of oxo ligands with different organic groups such as imido [13–16] or diazenido [17,18] or the coupling of lacunary POMs with organosilyl/germyl [19–21] organo-phosphoryl/phosphonates [22–28] and organotin derivatives [29–37].

These covalent functionalization strategies not only broaden the applications of POMs but also improve long-term stability, solubility, redox behavior, spectroscopic response and biological activities of the clusters as well as facilitating the construction of novel POM based functional materials [38–42].

About a decade ago, we started to systematically investigate the organic derivatization of Keggin $[PW_{11}O_{39}\{SnR\}]^{4-}$ and Dawson $[P_2W_{17}O_{61}\{SnR\}]^{7-}$ phosphotungstates bearing organotin side chains R with reactive groups [43–48]. This approach corresponds to what is now called postfunctionalization of POMs. In this context, it is highly desirable to have some standard reactions that can be applied to couple virtually any organic molecule to a POM. We have focused on amidation and CuAAC click chemistries that were applied to a broad range of organics. In order to diversify the inorganic moiety, we now investigated these reactions with $[SiW_{11}O_{39}\{SnR\}]^{5-}$ derivatives. This Keggin silicotungstate is smaller than our previous Dawson phosphotungstates, but with a higher charge than the $[PW_{11}O_{39}\{SnR\}]^{4-}$ analog. It would therefore be a valuable complementary compound for a number of applications, in particular those including POM based redox processes.

Pope prepared organotin derivatives of the monolacunary $[SiW_{11}O_{39}]^{8-}$, among those $Cs_5[SiW_{11}O_{39}\{Sn(CH_2)_2COOH\}]$ [36]. He also investigated some side chain reactivities (ester and nitrile hydrolysis), which demonstrated the hydrolytic stability of the POM-hybrid and he performed amide-coupling reactions on the organotin precursor. We show here the possibilities (i) to prepare an intramolecularly activated mixed anhydride from $[SiW_{11}O_{39}\{Sn(CH_2)_2COOH\}]^{5-}$ that allows residue-free coupling with amines and (ii) to perform CuAAC click chemistry on an azide derivative $[SiW_{11}O_{39}\{Sn(CH_2)_2CONH(CH_2)_3N_3\}]^{5-}$. This type of reactions is important for introducing the silicotungstate as redox label in different applications.

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2. Experimental

2.1. Materials and instrumentations

All the chemical compounds and reagents were purchased from Sigma Aldrich and used without further purification. Acetonitrile was dried and distilled over CaH_2. All reactions were carried out under argon atmosphere with magnetic stirring. The monovacant Keggin POM $K_8[\alpha\text{-}SiW_{11}O_{39}]$ was prepared as previously described [49].

FT-IR spectra were recorded from a Bruker Tensor 27 ATR diamond PIKE spectrophotometer. The ^1H and ^{13}C NMR spectra were respectively recorded at 400 and 100 MHz with a Bruker AVANCE 400. Chemical shifts are reported in ppm from TMS using the residual ^1H and ^{13}C solvent peaks as internal reference (δ = 7.26 and 77.2 ppm, respectively, for $CDCl_3$, δ = 2.50 and 39.5 ppm for DMSO-d_6, δ = 1.94 and 118.26 ppm for CD_3CN).

Mass spectrometry was carried out using an ion trap type Bruker Esquire (R = 3000) coupled to an electrospray source (ESI-MS) at the Paris Institute of Molecular Chemistry (IPCM). 50 μM POM solutions in CH_3CN were injected using a syringe pump with flow rate 160 μL min^{-1}. The detector was used in negative ion mode at a voltage of 3500 V. The voltage difference between the orifice and the skimmer is set at 45 V to avoid decomposition of the POMs. The LMCO (low-mass cutoff) of the ion trap was set at 80–140 in order to preferentially trap ions of higher m/z ratio.

All electrochemical measurements were carried out using an Autolab model PGSTAT 12 potentiostat/galvanostat controlled with the General Purpose Electrochemical System (GPES) software (Eco Chemie B.V., The Netherlands). A classical three electrode set up was used with a Ag/AgCl reference electrode, Pt wire counter electrode and glassy carbon electrode (with inner diameter of 3 mm), which were purchased from CHI Instruments,Inc. All the potentials are recorded with respect to the reference electrode. The diffusion coefficient was calculated using Randles–Sevcik equation [50] ($I_p = 2.69 \times 10^5 AD^{1/2} Cn^{3/2} V^{1/2}$), where I_p is for the peak current of the voltammograms, A is the electrode surface area (cm^2) D the diffusion coefficient, V is the scan rate (V s^{-1}), n the number of electrons.

2.2. Synthesis of $TBA_5[(SiW_{11}O_{39}\{SnCH_2CH_2CO_2H\}]$ (**1**)

Trichloro propionic acid (0.587 mmol) was added to a solution of TBABr (4.06 mmol) in 30 mL of acetonitrile and the lacunary Keggin POM, $K_8SiW_{11}O_{39}$ (0.409 mmol) was subsequently added. The mixture was stirred for 1 h at room temperature under argon. After the reaction time was completed the remaining solid was filtered off. Evaporation of the solvent resulted in a pale yellow oily solid, which was precipitated with acetone/ethanol/diethyl ether (1/1/excess) to give the desired product as a white solid. (92% yield). IR: ν = 2962 (m), 2947 (w), 2885 (m), 1728 (w), 1481 (m), 1388 (w), 1010 (s), 964 (s), 902 (s), 771 (vs) cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 1.03 (t, J = 8 Hz, 60H, $N(CH_2CH_2CH_2CH_3)_4$), 1.26 (m, 2H, $SnCH_2$), 1.39–1.51 (m, 40H, $N(CH_2CH_2CH_2CH_3)_4$), 1.64–1.75 (m, 40H, $N(CH_2CH_2CH_2CH_3)_4$), 2.69 (dd, J = 8.6, 7.1 Hz, 2H, $CH_2C{=}O$), 3.12–3.30 (m, 40H, $N(CH_2CH_2CH_2CH_3)_4$); ^{13}C NMR (100 MHz, CD_3CN): δ = 12.6 ($N(CH_2CH_2CH_2CH_3)_4$), 17.5 ($SnCH_2$), 19.1 ($N(CH_2CH_2CH_2CH_3)_4$), 23.1 ($N(CH_2CH_2CH_2CH_3)_4$), 28.8 ($CH_2C{=}O$), 58.0 ($N(CH_2CH_2CH_2CH_3)_4$), 175.2 ($C{=}O$).

2.3. Synthesis of $TBA_4[SiW_{11}O_{39}\{Sn(CH_2)_2C({=}O)\}]$(**2**)

To a solution of **1** in freshly distilled acetonitrile (25 mL) triethyl amine (2.2 equiv) and isobutyl chloroformate (1.2 equiv.) were added. The reaction mixture was stirred at room temperature overnight under argon. A cation exchange resin (Amberlyst 15, 16–50 mesh, TBA$^+$ form) was then added followed by addition of 10 mL acetone and the mixture was stirred for 1 h under rotary. The resin was filtered off and the filtrate concentrated under vacuum. The oil obtained was dissolved in acetone (7 mL) and precipitated by addition of ethanol (7 mL) and diethyl ether (30 mL) and the white solid was centrifuged and dried using a vacuum pump. A white fluffy powder was obtained in 91% yield. IR: ν = 2962 (m), 2947 (w), 2877 (m), 1735 (w), 1473 (m), 1388(w), 1226 (w), 1010 (s), 964 (s), 902 (s), 771 (vs) cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 1.01 (t, J = 8 Hz, 48H, $N(CH_2CH_2CH_2CH_3)_4$), 1.30–1.50 (m, 34H, $N(CH_2CH_2CH_2CH_3)_4 + SnCH_2$), 1.60–1.77 (m, 32H, $N(CH_2CH_2CH_2CH_3)_4$), 2.81 (m, 2H, $CH_2C{=}O$), 3.12–3.26 (m, 32H, $N(CH_2CH_2CH_2CH_3)_4$); ^{13}C NMR (100 MHz, CD_3CN): δ = 12.6 ($N(CH_2CH_2\ CH_2CH_3)_4$), 17.2 ($SnCH_2$), 19.1 ($N(CH_2CH_2CH_2CH_3)_4$), 23.1 ($N(CH_2CH_2CH_2CH_3)_4$), 30.8 ($CH_2C{=}O$), 57.8 ($N(CH_2CH_2CH_2CH_3)_4$), 168.7 ($C{=}O$).

2.4. Synthesis of $TBA_5[SiW_{11}O_{39}\{SnCH_2CH_2CONH(CH_2)_3N_3\}]$(**3**)

The product **2** was dissolved in 30 mL acetonitrile to which triethyl amine (1.2 equiv) and azidopropylamine (2 equiv) were added. The mixture was stirred at room temperature overnight. Cation exchange resin (Amberlyst 15, 16–50 mesh, TBA$^+$ form) was added followed by addition of 10 mL acetone and the mixture was stirred for 1 h under rotary. The resin was filtered off and the filtrate concentrated under vacuum. The oil obtained was dissolved in acetone (7 mL) and precipitated by addition of ethanol (7 mL) and diethyl ether (30 mL). The white solid was centrifuged and dried under vacuum (91% yield). IR: ν = 2962 (m), 2942 (w), 2877 (m), 2098 (m), 1658 (w), 1482 (m), 1380 (w), 1002 (s), 956 (s), 894 (s), 771 (vs) cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 0.98 (t, J = 8 Hz, 60H, $N(CH_2CH_2CH_2CH_3)_4$), 1.37–1.47 (m, 42H, $N(CH_2CH_2CH_2CH_3)_4 + SnCH_2$), 1.61–1.69 (m, 40H, $N(CH_2CH_2CH_2CH_3)_4$), 1.74–1.85 (m, 2H, $CH_2CH_2CH_2$), 2.49 (t, J = 8 Hz, 2H, $CH_2C{=}O$), 3.12–3.29 (m, 42H, $N(CH_2CH_2CH_2CH_3)_4 + NHCH_2$), 3.39–3.42 (m, 2H CH_2N_3), 7.01 (t, 1H, J = 8 Hz, NH); ^{13}C NMR (50 MHz, CD_3CN + 5% D_2O; repurified on cation exchange resin): δ = 12.7 ($N(CH_2CH_2CH_2CH_3)_4$), 19.1 ($N(CH_2CH_2CH_2CH_3)_4$), 19.2 ($SnCH_2$), 23.2 ($N(CH_2CH_2CH_2CH_3)_4$), 28.3 ($CH_2CH_2CH_2$), 31.9 ($CH_2C{=}O$), 36.1 ($NHCH_2$), 48.8 (CH_2N_3), 57.8 ($(CH_2CH_2CH_2CH_3)_4$), 174.0 ($C{=}O$).

2.5. Synthesis of $TBA_5[(SiW_{11}O_{39})\{Sn(CH_2)_2CONH(CH_2)_3(N_3C_2H)C_{10}H_9Fe\}]$(**4**)

To a solution of **3** (0.04 mmol) in acetonitrile (1 mL) was added ethynyl ferrocene (0.08 mmol, 2 equiv.). This was followed by subsequent addition of a solution of $CuSO_4{\cdot}5H_2O$ (0.04 mmol, 1 equiv) in water (1 mL) and a solution of sodium ascorbate (1.6 mmol, 40 equiv) in water (1 mL). The mixture was stirred at RT for 24 h. A cation-exchange resin (Amberlyst 15, 16–50 mesh, TBA$^+$ form) was added, followed by acetone (10 mL) and the mixture was stirred for 1 h or until the disappearance of the precipitate (if any appeared). The resin was filtered off and the filtrate was concentrated *in vacuo*. White powder residue was washed twice with water (10 mL) and isolated by centrifugation. After drying *in vacuo*, the residue was dissolved in acetone (2 mL) and precipitated by adding CH_2Cl_2/Et_2O (2 mL/30 mL). The new solid was isolated by centrifugation, washed with Et_2O and dried *in vacuo* and the desired POM was obtained as a white powder (81% yield). IR: ν = 2968 (m), 2958 (w), 2879 (m), 1664 (w), 1485 (m), 1388 (w), 1108 (s), 1002, 952 (s), 902 (s), 887 (s), 781 (vs) cm^{-1}; ^1H NMR (400 MHz, CD_3CN + 5% D_2O): δ = 1.00 (t, J = 8 Hz, 60H, $N(CH_2CH_2CH_2CH_3)_4$), 1.07–1.17 (m, $SnCH_2$), 1.40–1.49 (m, 40H, $N(CH_2CH_2CH_2CH_3)_4$), 1.64–1.72 (m, 40H, $N(CH_2CH_2CH_2CH_3)_4$), 2.30 (m, 2H, $CH_2CH_2CH_2$), 2.57 (m, 2H, $CH_2C{=}O$), 3.15–3.28 (m, 42H, $N(CH_2CH_2CH_2CH_3)_4 + NHCH_2$),