



Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Dawson-type polyoxometalate-based oligomeric Hg(II)-acetylide hybrid: Synthesis, characterization and materials properties

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ARTICLE INFO

Article history:

Received 23 December 2014

Received in revised form

17 February 2015

Accepted 24 February 2015

Available online xxx

Keywords:

Polyoxometalate

Inorganic-organic hybrid

Acetylide

Mercury

LB film

ABSTRACT

A new synthetic scheme for preparing Dawson-type polyoxometalate (POM) based inorganic-organic hybrid material is reported. A new heteropolytungstate-based oligomeric Hg(II) acetylide inorganic-organic hybrid compound (OHgOD) was prepared by Hagihara's dehydrohalogenating coupling of a diacetylene POM hybrid with diphosphoryl functionality and mercury(II) halide. This method provides a rigid covalent linkage between the POM and the organometallic Hg(II) acetylide moiety. The materials properties of hybrid LB film derived from the hybrid were studied.

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Introduction

Polyoxometalates (POMs) currently receive considerable research interest because of their wide range of properties and their significant applications in many fields such as analytical chemistry, catalysis, materials science, and medicine [1,2]. Among various metal-oxygen clusters, POMs are most attractive not only because of their structural versatility and rich optoelectronic properties but also because of their discrete molecular structures which allow surface functionalization in a controlled and rational way [3]. Indeed, a number of POM-containing organic-inorganic hybrids have recently been reported [4], among which a few examples involve POM-containing polymers.

Since the pioneering work of Peng, Wei and Errington on organic derivatives of Lindqvist POMs [5], Cronin and Song on organofunctionalized Anderson POMs [6], Proust and Izzet have developed phase transfer conditions applicable to the functionalization of mono- [7], di- [8], or tri-vacant POMs [9]. Recently, Odobel, Izzet, Nomiya and Villanneau reported a family of Dawson-type POMs di-functionalized with organo-silyl or organo-phosphoryl moieties [10]. Some synthetic tools using classical reactions such as Sonogashira and Huisgen couplings have been developed for organic synthesis and POM derivatization.

Rigid-rod organometallic polyynes of late transition metals represent an important class of new materials for basic and applied research [11]. As continuation of our research efforts [12,13] in this field and the application of POM-based hybrids in the development of photochemical devices, we started our work in grafting rigid, π -conjugated group 12 mercury(II) polyyne chains as photoactive antenna to the redox-active Dawson heteropolytungstate via classical CuI-catalyzed Hagihara's dehydrohalogenating coupling reaction. To our knowledge, there are no literature report on covalent post-functionalization of POMs with Hg(II)-acetylide groups by such dehydrohalogenating coupling reaction to form Hg–C bond.

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Such a methodology allows the connection of the POM to the organometallic entity via a rigid linker. Furthermore, this simple and efficient synthetic route can be extended to a large number of transition metal chromophores. We describe here the synthesis of a novel POM-based inorganic-organic hybrid oligomer by the covalent bonding of Hg(II)-acetylide units in oligomeric structure (Fig. 1). The material properties of hybrid LB film derived from the hybrid were studied.

Experimental section

Materials and instrumentation

Analytical grade solvents were purified by distillation over appropriate drying agent under an inert nitrogen atmosphere prior to use. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources and used without further purification. The compounds $K_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}] \cdot 20\text{H}_2\text{O}$ [14] and 4-ethynylphenyl phosphonic acid [15] were synthesized according to the published procedures. Infrared spectra were recorded from KBr pellets on a Nicolet iS10 FTIR spectrometer. ^1H and ^{31}P NMR spectra were recorded on a VARIAN 600 MHz NMR spectrometer, using deuterated solvents as the lock and reference. Chemical shifts were reported in ppm relative to SiMe_4 for ^1H and $85\% \text{H}_3\text{PO}_4$ for ^{31}P nucleus. Cyclic voltammetry at a carbon electrode was carried out using the ZAHNER IM6 system. A standard three-electrode cell was used, which consisted of the working vitreous carbon electrode, an auxiliary platinum electrode, and an aqueous saturated calomel electrode (SCE) equipped with a double junction. The scan rate was 200 mV s^{-1} . Each studied product was dissolved in distilled acetonitrile at a concentration of 10^{-4} M using TBAPF_6 as the electrolyte (10^{-1} M). The high performance triple quadrupole time-of-flight mass spectra were obtained using API QSTAR Pulsar/LC/MS/MS system mass spectrometer operated in the negative ion mode. C, H, N contents were determined by using a Vario Micro Cube elemental analyzer. Pt and W contents were determined by using an inductively coupled plasma (ICP) atomic absorption spectrometer (Optimal 8000, USA). UV–vis spectra were measured on a UNICAM He λ ios α spectrometer. PL spectra were recorded on a SPEX F212 fluorescence spectrometer. Surface photovoltage spectroscopy (SPS) was measured on a D-300 surface photovoltage instrument. Photoluminescence spectra were recorded on a SPEX F212 fluorescence spectrometer. Atomic force microscopy (AFM) image and scanning tunneling microscopy (STM) of the LB films were measured on a SPA-400 atomic force microscope.

Monolayer and LB film fabrication

OHgOD can be organized as a monolayer using the LB technique in which arachidic acid (AA) was used in ensuring a good-quality LB

film for OHgOD. Monolayer formation and deposition were carried out on a French LB 105 slot at $20 \pm 1 \text{ }^\circ\text{C}$ under a continuous dry nitrogen flow. The surface pressure was measured by the Wilhelmy plate method. Triple-distilled water at $\text{pH} = 6$ with a resistivity higher than $1.8 \times 10^5 \text{ } \Omega\text{m}$ and surface tension of 70 mN m^{-1} was used as the subphase. The spreading solution of OHgOD and AA (2:1, $1.0 \times 10^{-4} \text{ mmol L}^{-1}$) in the mixture of acetonitrile and chloroform (v/v, 1:2) was spread onto the pure water subphase using a microsyringe. Compression began at a compression rate of $0.3 \text{ cm}^2 \text{ min}^{-1}$ after the solvent was evaporated for 45 min and the isotherms were recorded. All the experiments for monolayer deposition were performed under a surface pressure of 5 mN m^{-1} . In the case where a stable Langmuir monolayer of OHgOD/AA film was formed on the subphase, the monolayer was subsequently deposited onto substrates [indium tin oxide (ITO) substrate for current–voltage (I – V) and SPS] by the vertical dipping method at a rate of 3 mm min^{-1} , resulting in a fairly good deposition of a typical Y-mode film. The number of layers of LB film prepared here is equal to the number of dipping or lifting processes, on each of which a floating Langmuir monolayer was transferred onto the substrate with a good transfer ratio of ca. 1.

Synthesis of OD

To a solution of 4-ethynylphenyl phosphonic acid (0.6 g, 1.6 mmol) in CH_3CN (50 mL) stirred at room temperature was added the solid $K_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}] \cdot 20\text{H}_2\text{O}$ (2 g, 0.4 mmol) and the solid NBu_4Br (1.68 g, 5.2 mmol). After 15 min, 1.24 M HCl (1.3 mL) was added to the mixture to adjust the pH to 2. After refluxing the mixture for 2 h, the mixture was cooled to room temperature and the light yellow product was filtered, washed vigorously with ethanol and water, and dried with diethyl ether to yield OD (2.08 g, 0.32 mmol, 80%) as a light yellow powder. ^1H NMR (DMSO-d_6) $\delta = 7.94$ – 7.98 (m, 4H, ArH), 7.55 – 7.57 (m, 4H, ArH), 4.36 (s, 2H, CH), 3.16 (t, $J = 20.5 \text{ Hz}$, 48H, CH_2N), 1.55 – 1.59 (m, 48H, $\text{CH}_2\text{CH}_2\text{N}$), 1.32 (sextuplet, $J = 20.5 \text{ Hz}$, 48H, CH_2CH_3), 0.93 (t, $J = 20.5 \text{ Hz}$, 72H, CH_3). ^{31}P NMR (CD_3CN) $\delta = 14.97$ (m, $\text{P}(\text{O})$), -10.14 (s, PW_8), -11.70 ppm (s, PW_9). IR (KBr, cm^{-1}) $\nu = 3254$ (s), 3063 (s), 2106 (w), 1146 (w), 1110 (w), 1092 (vs), 1043 (s), 1030 (w), 975 (vs), 921 (vs), 905 (vs), 819 (vs), 809 (vs), 740 (vs).

Synthesis of OHgOD

OD (80.7 mg, 0.0136 mmol) was dissolved in CH_3CN (5 mL) and HgCl_2 (3.8 mg, 0.0136 mmol), CuI (3 mg) and Et_3N (0.1 mL) were subsequently added. After stirring at room temperature for 12 h, all the volatile compounds were removed under reduced pressure. The residue was redissolved in CH_3CN and filtered. Diethyl ether (30 mL) was added to the filtrate, and a pale yellow precipitate appeared. The crude solid was recovered by centrifugation. For

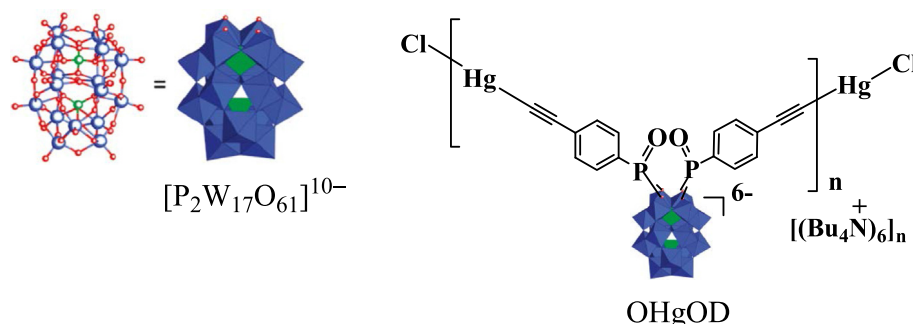


Fig. 1. Structure of OHgOD.

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