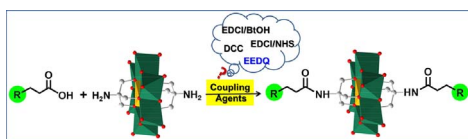


# A survey of the influence of EEDQ on efficient post-functionalization of an Anderson-type polyoxomolybdate towards construction of organic-inorganic hybrids

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## GRAPHICAL ABSTRACT



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## ABSTRACT

In the present work, 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) was used as an effective coupling agent to design and synthesize a diversity of post-functionalized polyoxomolybdate (POM) hybrids based on an Anderson-type POM cluster and incorporating various organic molecules. Subsequently, the synthesized hybrids were characterized via various analytical and spectroscopic techniques including FT-IR spectroscopy, ESI-MS, <sup>1</sup>H NMR spectroscopy, and elemental analysis. The present investigations revealed that different factors such as alkyl chain length, steric effect and electrophilicity had a profound effect on the post-functionalization of the Anderson-type POM cluster utilizing EEDQ as the coupling agent. By extensively investigating the effect of EEDQ on the efficient post-functionalization of an Anderson-type POM cluster, EEDQ can be more effectively utilized for post-functionalizing the POM clusters towards the future construction of various organic-inorganic hybrids.

## 1. Introduction

Hybrid organic-inorganic materials, constructed by covalently linking the organic component and the inorganic cluster together, are one of the most significant fields of investigation in supramolecular chemistry and material science [1–3]. The synthesis of novel organic-inorganic hybrids has led to the development of hybrid organic-inorganic materials, in which not only the functions of both organic and inorganic components are perfectly maintained, but also creating synergistic effects make the comprehensive properties and performances of hybrid materials much better than the individual component [4–6].

Polyoxometalates (POMs), a well-known class of early transition metal-oxygen clusters, have been extensively studied for their potential widespread applications in various fields such as catalysis, material

science, biology, medicine and electrochemistry [7–10]. Due to the specific properties, versatile structures and various shapes of POMs, the construction of POM-based organic-inorganic hybrids have attracted significant research interest in recent years [11–17]. Among the organic-POM hybrids constructed by covalent or non-covalent modifications, much attention has been devoted to developing covalently linked organic-POM hybrids by considering hybridization at the molecular level and possible synergistic effects between the organic component and the POM cluster. For this reason, numerous Dawson-, Anderson-, Keggin-, and Lindqvist-type POMs have been utilized to synthesize the covalently linked organic-POM hybrids, and the properties and possible applications have been studied [18–24]. Compared to the other POM types, the Anderson-type POM exhibits both a fascinating symmetrical structure and biological properties. Consequently, the Anderson-type

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POM has received more research attention and has been employed as an ideal building block for constructing organic-POM hybrids possessing a deeper orientation toward appealing structures and functionalization [25–30]. To date, many organic molecules, such as aromatic compounds [31,32], alkyl chains [33], ferrocene [34,35], porphyrin [36], cholesterol [37,38], azobenzene [39], adenine [40], and coumarin [41] have been grafted onto the Anderson-type POM cluster, leading to promising organic-POM hybrids with outstanding properties and wonderful performance attributed to the synergistic effects between the organic components and the POM cluster.

Notably, the covalent modification of the Anderson-type POM cluster with organic molecules has been limited and remains a challenging task due to the strong electrophilicity of the POM cluster, which greatly lowers the reactivity of the organic groups. To overcome this obstacle, many efforts have been contributed to the synthesis of organic-POM hybrids by employing various methods, mainly including using the tris(hydroxymethyl)aminomethane (tris) esterification reaction [31,34,35,42,43], the actively coupling agent [44], the copper catalyzed azide-alkyne cycloaddition (CuAAC) reaction [45,46], the metal-free Diels-Alder click reaction [47], and the Sonogashira-Hagihara cross coupling reaction [48]. For instance, Hasenknopf et al. reported the first synthesis of an organic-POM hybrid using the tris-ligand esterification reaction, providing the first synthetic approach to covalently modify Anderson-type POM cluster with organic molecules [26,49]. Since then, synthetic attempts have dramatically been extended to the creation of organic-POM hybrids based on the Anderson-type POM cluster, and a growing number of examples have been reported by Cronin et al., Wu et al., and Wang et al. [31–33,39,40,50,51]. Recently, the Parac-Vogt group introduced the CuAAC reaction as an important synthetic approach into the Anderson-type POM system [46]. Obviously, introducing click chemistry into POM-based systems has become an important strategy to construct hybrid organic-inorganic materials with controlled properties. Despite these recent advances, there is still no general method to construct organic-POM hybrids between POM clusters and any organic molecule, since each method has its scope and limitation. Therefore, it is still meaningful and necessary to thoroughly investigate POM functionalization methods.

Herein, we employed the tris-modified Anderson-type POM  $\{[(n\text{Bu})_4\text{N}^+]_3(\text{MnMo}_6\text{O}_{18})^{3-}[(\text{OCH}_2)_3\text{CNH}_2]_2\}$  (Tris-POM-Tris), where two amino groups are connected onto two sides of the POM cluster. Considering both the well-known potent antitumor activity, and the potential use in further organic modifications for Tris-POM-Tris [25–27], we decided to evaluate the influence of coupling agents on the efficient post-functionalization of the tris-modified Anderson-type POM towards constructing organic-inorganic hybrids.

## 2. Experimental section

### 2.1. Materials

2-Ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ), 1-hydroxybenzotriazole (BtOH), (3-dimethylaminopropyl)ethylcarbodiimide monohydrochloride (EDCI), *N*-hydroxysuccinimide (NHS) and *N,N'*-dicyclohexylcarbodiimide (DCC) were purchased from Alfa Aesar. Aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS) was purchased from Hybrid Plastics as crystalline powders. All other reagents were purchased from J&K and all reagents were used as received. All solvents were purchased from commercial sources and used without further purification except acetonitrile ( $\text{CH}_3\text{CN}$ ) was used after fresh distillation.  $\{[(n\text{Bu})_4\text{N}^+]_3(\text{MnMo}_6\text{O}_{18})^{3-}[(\text{OCH}_2)_3\text{CNH}_2]_2\}$  was synthesized according to the literature [49].

### 2.2. Methods

$^1\text{H}$  NMR spectra were recorded on a Varian UNITY plus-400

spectrometer in dimethyl- $d_6$  sulfoxide ( $\text{DMSO}-d_6$ ). Multiplicities are indicated by the following abbreviations: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan LCQ advantage mass spectrometer. Fourier transformation infrared spectra (FT-IR) were recorded on a FT-IR spectrometer (Bio-Rad FTS-135) using the KBr pellet technique. Elemental analyses were performed using the Elementar (vario EL CUBE).

### 2.3. Synthesis of hybrids 1–4

**Synthesis of hybrid 1a.** To a 250 mL round-bottomed flask equipped with a condenser and a magnetic stirrer was added 3-maleimidopropionic acid [52] (2.2 equiv) and EEDQ (2.8 equiv), followed by addition of  $\text{CH}_3\text{CN}$ . The solution was stirred and refluxed at  $81^\circ\text{C}$ , and after 30 min, Tris-POM-Tris (1.0 equiv.) was added to the solution. The reaction mixture was additionally refluxed for 24 h. The reaction was then cooled to room temperature, and concentrated to the minimum. The concentrated liquid was added dropwise to tetrahydrofuran, giving a light orange solid. The crude product was redissolved in a small amount of  $\text{CH}_3\text{CN}$ . After a two-day evaporation of the solution in diethyl ether vapor at room temperature, a pure hybrid 1a was prepared (yield: 81%). FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3366, 2957, 2932, 2872, 1706, 1536, 1478, 1370, 1321, 1229, 1116, 1073, 1025, 940, 920, 902, 669, 564. ESI-MS (negative mode, DMF):  $m/z$  (%) 1701.4  $[\text{M} - 2\text{TBA} + \text{H}]^-$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  0.93 (t, 36H, TBA), 1.31 (m, 24H, TBA), 1.57 (m, 24H, TBA), 2.71 (m, 4H,  $\text{NCH}_2$ ), 3.15 (m, 24H, TBA), 3.56 (m, 4H,  $\text{CH}_2\text{CO}$ ), 7.01 (s, 4H, CH). Anal. Calcd for  $\text{C}_{70}\text{H}_{134}\text{MnMo}_6\text{N}_7\text{O}_{30}$ : C 38.49, H 6.18, N 4.49; found C 38.66, H 5.82, N 4.38.

**Synthesis of hybrid 1b.** The synthesis route for hybrid 1b is similar to that of hybrid 1a, except that the concentrated liquid was added dropwise to ethyl acetate (yield: 81%). FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3295, 2959, 2934, 2872, 1686, 1602, 1506, 1482, 1378, 1310, 1242, 1183, 1115, 1068, 1027, 940, 920, 903, 850, 810, 669, 564. ESI-MS (negative mode, DMF):  $m/z$  (%) 848.6  $[\text{M} - 3\text{TBA} + \text{H}]^{2-}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  0.92 (t, 36H, TBA), 1.31 (m, 24H, TBA), 1.56 (m, 24H, TBA), 1.99 (m, 4H,  $\text{CH}_2$ ), 2.59 (m, 4H,  $\text{CH}_2$ ), 3.16 (m, 24H, TBA), 3.35 (m, 4H,  $\text{CH}_2$ ), 7.46 (s, 2H,  $\text{NHCO}$ ), 7.96, 7.98 (d, 2H, Benzene-H), 8.05 (m, 2H, Benzene-H), 8.13 (m, 4H, Benzene-H), 8.24 (m, 6H, Benzene-H), 8.35 (s, 4H, Benzene-H). Anal. Calcd for  $\text{C}_{96}\text{H}_{152}\text{MnMo}_6\text{N}_5\text{O}_{26}$ : C 47.59, H 6.32, N 2.89; found C 47.94, H 6.63, N 2.79.

**Synthesis of hybrid 1c.** The synthesis route for hybrid 1c is similar to that of hybrid 1a except that the concentrated liquid was added dropwise to dichloromethane (yield: 82%). FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3291, 2959, 2937, 2873, 1691, 1551, 1484, 1458, 1378, 1332, 1257, 1155, 1027, 1025, 939, 920, 903, 671, 564. ESI-MS (negative mode, DMF):  $m/z$  (%) 804.6  $[\text{M} - 3\text{TBA} + \text{H}]^{2-}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  0.93 (t, 36H, TBA), 1.32 (m, 28H, TBA,  $\text{CH}_2$ ), 1.48 (m, 4H,  $\text{CH}_2$ ), 1.57 (m, 28H, TBA,  $\text{CH}_2$ ), 2.38 (m, 4H,  $\text{CH}_2$ ), 2.83, 2.86 (dd, 2H, CH), 3.16 (m, 28H, TBA, CH), 4.14 (t, 2H, CH), 4.29 (t, 2H, CH), 6.28 (s, 1H, NH), 6.38 (s, 1H, NH). Anal. Calcd for  $\text{C}_{76}\text{H}_{152}\text{MnMo}_6\text{N}_9\text{O}_{28}\text{S}_2$ : C 39.10, H 6.56, N 5.40; found C 39.42, H 6.84, N 5.37.

**Synthesis of hybrid 1d.** The synthesis route for hybrid 1d is similar to that of hybrid 1a except that the concentrated liquid was added dropwise to ethyl acetate (yield: 79%). FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3288, 2959, 2931, 2872, 1737, 1682, 1472, 1340, 1252, 1116, 1028, 940, 924, 902, 673, 563. ESI-MS (negative mode, DMF):  $m/z$  (%) 1979.7  $[\text{M} - 2\text{TBA} + \text{H}]^-$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  0.93 (t, 36H, TBA), 1.30 (m, 24H, TBA), 1.56 (m, 24H, TBA), 2.44 (m, 4H,  $\text{COCH}_2$ ), 2.76 (m, 4H,  $\text{CH}_2\text{COOH}$ ), 3.16 (m, 24H, TBA), 6.14 (s, 4H,  $\text{CH}_2\text{OCO}$ ), 7.54 (m, 4H, Benzene-H), 7.69 (s, 4H, Benzene-H), 8.13 (d, 4H, Benzene-H), 8.37 (d, 4H, Benzene-H), 8.70 (s, 2H, Benzene-H). Anal. Calcd for  $\text{C}_{94}\text{H}_{152}\text{MnMo}_6\text{N}_5\text{O}_{30}$ : C, 45.84; H, 6.22; N, 2.84. Found: C, 45.44; H, 6.70; N, 2.72.

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