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Polyoxometalates

Multivalent Recognition of Concanavalin A by {Mo_{132}} Glyconanocapsules—Toward Biomimetic Hybrid Multilayers

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Dedicated to Professor Achim Müller on the occasion of his 76th birthday

Abstract: Herein, we consider Müller's spherical, porous, anionic, molybdenum oxide based capsule, $(NH_4)_{42}$-$[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(CH_3COO)\}_{30}]\cdot 10\,CH_3COONH_4\cdot 300\,H_2O \equiv (NH_4)_{42}$·**1a**·crystal ingredients ≡ **1**, {Mo_{132}}, as an effective sugar-decorated nanoplatform for multivalent lectin recognition. The ion-exchange of NH_4^+ ions of **1** with cationic-sugars, D-mannose-ammonium chloride (**2**) or D-glucose-ammonium chloride (**3**) results in the formation of glyconanocapsules $(NH_4)_{42-n}\mathbf{2}_n$·**1a** and $(NH_4)_{42-m}\mathbf{3}_m$·**1a**. The Mannose $(NH_4)_{42-n}\mathbf{2}_n$·**1a** capsules bind selectively Concanavalin A (Con A) in aqueous solution, giving an association avidity constant of $K_a^{multi} = 4.6\times10^4\ M^{-1}$ and an enhancement factor of $\beta = K_a^{multi}/K_{ass}^{mono} = 21.9$, reminiscent of the formation of "glycoside clusters" on the external surface of glyconanocapsule. The glyconanocapsules $(NH_4)_{42-n}\mathbf{2}_n$·**1a** and $(NH_4)_{42-m}\mathbf{3}_m$·**1a** self-assemble in "hybrid multilayers" by successive layer-by-layer deposition of $(NH_4)_{42-n}\mathbf{2}_n$·**1a** or $(NH_4)_{42-m}\mathbf{3}_m$·**1a** and Con A. These architectures, reminiscent of versatile mimics of artificial tissues, can be easily prepared and quantified by using quartz crystal microgravimetry (QCM). The "biomimetic hybrid multilayers" described here are stable under a continual water flow and they may serve as artificial networks for a greater depth of understanding of various biological mechanisms, which can directly benefit the fields of chemical separations, sensors or storage-delivery devices.

Introduction

Biological membranes present dense areas of carbohydrates (glycocalyx) that play a fundamental role in cell–cell recognition processes through the multivalent binding of lectins.[1–3] The enhancement in the activity beyond what would be expected due to the increase in local sugar density is known as the "cluster glycoside effect".[4] Based on this understanding, many artificial multivalent carbohydrate-clustering systems have been reported.[5–20] Early evidence was observed by the group of Kiessling, using mannose-based polymers displaying inhibition of Concanavalin A (Con A) of erythrocytes.[5] Since then, molecular, dendrimeric or polymeric systems of increasing complexity have been extensively developed.[6] Up-scaled nanosystems like fullerenes,[7] metallosupramolecular spheres,[8] nanoparticles,[9–13] monolayers,[14] carbon nanotubes[15] and vesicles[16–20] have been used to generate multivalent carbohydrate nanoplatforms. Conclusions from these investigations typically reveal that multivalent binding is strongly dependent on the dynamic distribution of glycoside clusters self-assembled on the nanoplatform surface and vice versa. Within this context, the development of novel nanoscaled glycosystems[21–24] could provide new important insights into dynamic constitutional behaviour of glycocluster formation upon multivalent binding to lectins, observed in most of the biological scenarios.

Herein we consider Müller's spherical, anionic, molybdenum oxide based capsule, {Mo_{132}}: $(NH_4)_{42}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}$-$\{Mo^{V}_2O_4(CH_3COO)\}_{30}]\cdot 10\,CH_3COONH_4\cdot 300\,H_2O \equiv (NH_4)_{42}$·**1a**·crystal ingredients ≡ **1**,[25] which we hypothesised to be a potential nanoplatform of interest for sugar-cluster formation for lectin multivalent recognition. This capsule exhibits an advantage as a biomimetic nanocontainer in that it mimics the cell in terms of ionic/molecular exchanges with external media. Our goals are to quantify the glyconanocapsule–lectin interactions and to survey the formation of interconnected networks of glyconanocapsules through biomimetic protein–carbohydrate interactions. They may offer realistic interpretations close to in vivo tissue scenarios, which can also directly benefit the fields of chemical separations, sensors or storage-delivery devices.

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