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Water dispersible supramolecular assemblies built from luminescent hexarhenium clusters and silver(I) complex with pyridine-2-ylphospholane for sensorics

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ABSTRACT

The work introduces regularities and driving forces of self-assembly of hexarhenium clusters $[\{Re_6S_8\}L_6]^{n-}$ ($L = SO_3^{2-}, CN^-, OH^-$) with $[AgL']^+$ (L' = pyridine-2-ylphospholane) produced by dissociation of $[Ag_2L'_2]^{2+}$ in aqueous solutions. The formation of nano-sized Re_6—Ag assemblies is detected by the spectral measurements in the solutions and by the solid-state analysis of the separated colloids. The nature of L is highlighted as the main factor affecting the assembly. The poor affinity of the SO_3^{2-} ligands to Ag^+ restricts the assembly of $[\{Re_6S_8\}(SO_3)_6]^{10-}$ with the silver(I) complexes. $[\{Re_6S_8\}(OH)_6]^{4-}$ is more promising candidate for the heterometallic assembly contributed by both counter-ion binding and coordination bonds, while the efficient coordination of Ag^+ *via* the nitrogen of the cyanide ligands of $[\{Re_6S_8\}(CN)_6]^{4-}$ is the main driving force for the Re_6—Ag assembly. The stronger impact of $[Ag_2L'_2]^{2+}$ relative to Ag^+ cations on the formation of Re_6—Ag assemblies in aqueous solutions, as well as the presence of L' in the separated colloidal phase, indicate the important role of the L' ligand in the studied supramolecular systems. The cluster-centered luminescence serves as signaling system at the binding of glutathione, cysteine and dithiothreitol with Ag^+ ions of the heterometallic assemblies. The assemblies based on $[\{Re_6S_8\}(CN)_6]^{4-}$ are able to discriminate glutathione *versus* cysteine, while the assemblies formed by $[\{Re_6S_8\}(OH)_6]^{4-}$ give the unselective luminescence response on the both biothiols at the concentration level of 2 μM.

1. Introduction

Supramolecular self-assembly of ionic metal complexes in aqueous media is the well-known route for development of functional water dispersible nanomaterials for different applications, including contrast agents and sensors [1–9].

In particular, the development of nanosensors requires the inclusion of both sites for binding the required substrates, and a system that signals the presence of these bound species. Literature data exemplify the embedding of the metal ions into fluorescent organic nanoparticles as binding sites for some anionic substrates, while the organic molecules assembled into the nanoparticles serve as signaling system [10–12]. Since a plenty of water-soluble luminescent metal complexes can serve as signaling systems, their controlled self-assembly with metal ions as binding sites for substrates can result in water dispersible heterometallic supramolecular assemblies producing substrate-responsive luminescence. Thus, driving forces and limitations of the self-assembly in aqueous solutions resulting in the assemblies exhibiting substrate-responsive luminescence are the focus of the present work.

Hexarhenium chalcogenide cluster complexes have gained great attention during recent decades. Their unique structure with kinetically inert rigid cluster core $\{Re_6Q_8\}^{2+}$ ($Q = S^{2-}$ or Se^{2-}) is a reason for excellent luminescent properties [13–18], while perfect water solubility of the anionic hexarhenium clusters $[\{Re_6Q_8\}L_6]^{n-}$ makes them challenging basis for sensing. The tuning of the cluster-centered luminescence by external stimuli is exemplified by $[\{Re_6Q_8\}(OH)_6]^{4-}$, where apical ligand exchange results from the protonation phenomenon [19], but, commonly, sensing ability of the hexarhenium clusters is limited by slow exchange of six apical ligands (L). It is also well known that $[\{Re_6Q_8\}L_6]^{n-}$ anions form a great diversity of supramolecular heterometallic structures based on the coordination of apical ligands with metal ions or metal complexes [16,20–24]. Moreover, coordinated

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