



Photoinduced charge transfer in the supramolecular structure based on toroid polyoxomolibdate Mo_{138} and xanthene dye – Rhodamine-B



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ARTICLE INFO

Article history:

Received 19 June 2015

Received in revised form 25 July 2015

Accepted 29 July 2015

Available online 14 August 2015

Keywords:

Supramolecular structure

Charge transfer

Polyoxomolybdate

Vibration spectroscopy

DFT calculation

Luminescence

ABSTRACT

The new supramolecular structure based on the toroid nanoclustered giant polyoxomolybdate (POM) Mo_{138} and xanthene dye (rhodamine-B) was synthesized by a self-assembly technique in solution and was extracted in the solid state for the first time. Fluorescence studies of this structure have shown a very effective energy transfer (conditioned by the charge transfer and/or fluorescence resonance energy transfer mechanisms) from a dye molecule to a nanocluster under excitation by visible light (522 and 558 nm). The promotion of potential catalytic properties of polyoxomolybdate or revealing nonlinear optical properties could be expected there due to the presence of Mo^V and Mo^{VI} sites in Mo_{138} . Raman-spectroscopy showed significant changes for vibrating bands of the rhodamine-B conditioned by the energy transfer. Investigations of the supramolecular structure by zeta-potential and size distribution measurements allowed us to determine an interaction mechanism between the components in solution. Spatial location of dye molecules on the polyoxomolybdate surface and the integrity of nanocluster Mo_{138} in the supramolecular structure were found by FTIR-spectroscopy. The calculation of HOMO–LUMO electron transition of rhodamine-B by the Time-Dependent Density Functional Theory (TDDFT) technique revealed the potential overlapping between molecular orbitals of adsorbed dye molecules and POM's surface. That is well-correlated with the overlapping of fluorescence and absorption spectrums of rhodamine-B and the nanocluster respectively.

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1. Introduction

The giant nanoclustered polyoxomolybdates (POM) Mo_{138} , Mo_{154} and Mo_{132} structures are based on the coordinating oxygen polyhedrons of molybdenum connected through the common corners and edges. These structures are very complex with a highly symmetric type: ring-shaped (toroid) or fullerene-like (keplerate, buckyball) [1–3]. This results in the specific electron properties such as catalytic activities in respect to some UV-controlled oxidation organic reactions [4] and reciprocal stabilization of the POM-Polymer (PVA, PVP) ion-associates under UV-irradiation [5]. The POM are produced from an aqueous solution by the self-assemble technique that reveals an easy way to use them in commercial

applications. One of the first discovered polyoxomolybdates is the toroid nanocluster Mo_{154} , consisting of the coordinating oxygen octahedrons and pentagonal bipyramids of $\text{Mo}^V/\text{Mo}^{VI}$ connected through the common corners and edges [2]. For this work we chose the nanocluster Mo_{138} which has the specific electron state owing to its defect structure concerning Mo_{154} , which is stabilized by the bidentate ligands (acetate groups – Ac) [2]. The chemical compound of nanocluster Mo_{138} is shown by the formula: $(\text{NH}_4)_{32}[\text{Mo}_{110}^V\text{Mo}_{28}^V\text{O}_{416}\text{H}_6(\text{H}_2\text{O})_{58}(\text{CH}_3\text{COO})_6] \cdot x\text{H}_2\text{O}$ ($x \approx 250$) or as the schematic description – $[\{\text{Mo}_2\}_6\{\text{Mo}_2\text{Ac}\}_2\{\text{Mo}_8\}_{10}\{\text{Mo}_8\text{Ac}\}_4\{\text{Mo}_1\}_{10}]^{32-}$ [2]. In the nanocluster Mo_{138} the presence of Mo^V centers should lead to paramagnetic activities but the lifetime of these valence states is very short due to high electron's delocalization and it could not be detected by EPR spectroscopy [5]. This mobility of valence electrons promises interesting properties to Mo_{138} for some redox reactions. Moreover, the nanocluster Mo_{138} is readily dissolved in water forming a multicharged (minus 32) polyoxoanion such as Mo_{154} [6]. In their turn, polyoxoanions can spontaneously aggregate into hollow, single-wall, spherical globules, their diameter reaching ca. 100 nm in solution [7–9]. That is a good ability to the

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purposeful design of some new self-assembling supramolecular systems based on this property [9].

We suggest a strategy directed to formation of ion-associates (based on the Mo_{138}) with a charge transfer by the functionalization of nanocluster's surface in solution by rhodamine-B (RhB). In its turn, that allows us to realize a light-controlled promotion of the potential catalytic activities of Mo_{138} for homogeneous and heterogeneous redox reactions. The ability of the energy transfer (especially the charge transfer) in this system is conditioned by the overlapping of the emission and the absorption spectrums of the rhodamine-B (donor) and the nanocluster Mo_{138} (acceptor) respectively.

As a result of our research, we report that the new supramolecular system based on ion-associates $\text{Mo}_{138}\text{-(RhB)}_n$ was created in an aqueous solution, was extracted to a solid state and was characterized by FTIR, Raman, UV-Vis and Fluorescence spectroscopies for the first time. The model of the interaction between Mo_{138} and dye molecules depending on the components ratio was created by measuring of the zeta-potential and the average diameter in an aqueous solution. Spectroscopy studies of ion-associates $\text{Mo}_{138}\text{-(RhB)}_n$ by FTIR-spectroscopy allowed us to determine the adsorbed dye molecules' location and the role of the carboxyphenyl group of RhB molecule for interaction with the nanocluster surface. Fluorescence studies showed the photoinduced energy transfer in ion-associates, where the role of charge transfer mechanism was found by UV-Vis spectroscopy and by the TDDFT calculation of the *HOMO/LUMO*-orbitals types of RhB.

2. Experimental

2.1. Synthesis

Polyoxomolybdate Mo_{138} was produced using the method described elsewhere [2]. For that production stage, by consistent mixing of ammonium heptamolybdate, acetic acid and hydrazinium sulfate, an aqueous solution was prepared and, in three weeks, Mo_{138} crystals were filtered. Primarily, using this method, the obtained products were standardized by German scientists led by Professor A. Müller using the following methods: monocrystal X-ray diffraction analysis; resonance Raman and IR-spectroscopy; UV-Vis spectroscopy, and element analysis [2]. The samples obtained by our group earlier were also analyzed by the physicochemical methods group to confirm the nanoclustered structure [5], utilising IR and Raman spectroscopy, element analysis, UV-Vis spectroscopy, and NMR spectroscopy (on ^1H and ^{13}C). To produce the solutions we used fresh distilled water. All fresh-produced solutions of Mo_{138} were used only in one 24 h period.

The supramolecular system based on ion-associates $\text{Mo}_{138}\text{-(RhB)}_n$ was prepared by mixing the corresponding aliquots of the starting solutions of pure components: Mo_{138} and rhodamine-B. After that the total solution volume was brought by distilled water to the bottle measuring mark.

The extraction of the supramolecular system to a solid state was carried out by the centrifugation (10000 rpm) of an aqueous solution at components ratio referring to the isoelectric point.

2.2. Zeta-potential and average diameter measures

The working concentration (4.26×10^{-6} mol/l \approx 0.11 g/l) of POM Mo_{138} was chosen according to our data of its stability in solution [5]. The measurements of zeta-potential and the average diameter were carried on the series of aqueous solutions containing POM Mo_{138} and the rhodamine B in different molar ratios. These solutions were prepared by mixing the corresponding aliquots of the starting solutions of pure components, after that the

total solution volume was brought by distilled water to the bottle measuring mark. We use the following molar components ratios: 1/1, 1/3, 1/5, 1/7, 1/10, 1/15, 1/20, 1/25, 1/30. The analysis of the dependence of the size distribution and the zeta-potential on the ion-associate composition was carried out by "Zetasizer Nano Z" (Malvern) in solution.

2.3. Spectral analysis

To control the purity of Mo_{138} after synthesis the IR-specter was measured by IR-Fourier spectrometer Nicolet 6700 (Thermo Scientific) in the FTIR mode. The specter' series of pure components (Mo_{138} and RhB) and supramolecular system extracted to a solid state were measured by IR-Fourier spectrometer Spectrum One (Perkin Elmer) in the diffuse reflection mode. The Raman-specters were measured by Confocal Raman Microscope and Raman Imaging System ALPHA300AR (WITec Instruments Corp.) at a solid state at the laser wavelength of 488 nm. In solution charge transfer studies were carried out by using the Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies).

2.4. The quantum mechanical calculation of *HOMO* and *LUMO* for Rhodamine-B

The calculation of the geometry optimization and of the *HOMO/LUMO* configuration for dye molecules was carried out by the Time-Dependent Density Functional Theory (TDDFT) technique in the software environment «GAMESS» [10]. For calculation of the geometry optimization and the configuration of the molecular orbitals we used the "def2-TZVP" basis set.

3. Results and discussion

3.1. Interaction model in solution – zeta-potential and the average diameter

In the aqueous solution nanocluster Mo_{138} and rhodamine-B dissociate producing the multi-charged polyoxoanion and the single-charged cationic form respectively. The positive charge of RhB is located on the one of two nitrogen atoms forming the mesomeric structure. Thus, the interaction between nanocluster POM Mo_{138} and dye molecules commonly occurs by the electrostatic force. But the dye molecules (RhB) do not interact with individual POM because the polyoxoanions of Mo_{138} spontaneously form spherical hollow globules stabilized by the NH_4^+ cations and hydrogen bond [7] in an aqueous solution. The average diameter of globules is close to 100 nm based on the dynamic light scattering (DLS) measurement at POM concentration in solution is 4.26×10^{-6} mol/l and the zeta-potential is approximately -40 mV. Therefore, this interaction process can be described by the model of the electric double layer (EDL) for the interaction of a negatively charged surface and two types of single-charged cations. In the context of that, dye molecules exchange NH_4^+ cations in a compact layer of EDL as the RhB concentration is increasing. However, there are some differences from a simple model. Firstly, due to the fact that the dye molecule's diameter (1.3 nm at a longer dimension) is smaller than POM inner pore diameter (2.0 nm), it can lead to the penetration of RhB into a hollow globule and to the interaction of dye molecules with the inner side of POM's globules. Thus, these interacted dye molecules do not cause the changes in the measured zeta-potential significantly. Secondly, rhodamine-B molecule consists of three rigidly connected aromatic rings and a carboxyphenyl group, which are placed in a different plane. That makes the steric factor important for interaction between Mo_{138} and RhB.

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