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The supramolecular system with Nonreversible Resonance Energy Transfer based on the toroidal nanocluster Mo₁₃₈ and xanthene dye – Rhodamine B

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Fig. The ion-associate Mo₁₃₈-(Rhodamine-B)_n

The new supramolecular system based on the toroid nanoclustered giant polyoxomolybdate (POM) Mo₁₃₈ and the xanthene dye Rhodamine B (RhB) was produced by the self-assembly method in solution and solid state. For the first time it was characterized by different physicochemical methods. The composition of Mo₁₃₈ nanocluster is presented by the formula: (NH₄)₃₂[Mo^{VI}₁₁₀Mo^V₂₈O₄₁₆H₆(H₂O)₅₈(CH₃COO)₆] \cdot xH₂O ($x \approx 250$). In aqueous solution the Mo₁₃₈ forms multicharged anion. In turn they spontaneously aggregate to hollow, single-wall, spherical globules (diameter is \sim 300 nm depending on POM concentration and pH) which are stabilized by the NH₄⁺ cations and hydrogen bonds. The interaction between positively charged RhB and globular surface is conditioned by the electrostatic force, as a result the ion-associates Mo₁₃₈-(RhB)_n are formed. That leads to a decrease in the zeta-potential value of the supramolecular system from minus 45 mV (for pure Mo₁₃₈) to zero at the isoelectric point which corresponds to the ratio of components Mo₁₃₈ : RhB = 1 : 35 in solution (Mo₁₃₈ concentration is $4.26 \cdot 10^{-6}$ mol/l). At this conditions the average diameter of the supramolecular globular structure passes through minimum from 116 nm (globular diameter in pure Mo₁₃₈ solution) to 82 nm (minimum point) that is conditioned by compression of the electric double layer due to addition of RhB. By the consecutive washing (ethanol/water) and centrifugation, the produced supramolecular system (at Mo₁₃₈ : RhB = 1 : 35) was deposited and dried in air. As a result the FTIR-spectrum analysis of this sample revealed the planar arrangement of RhB molecules on the POM surface. The UV-Vis spectrums showed the significant long-wavelength shift of the RhB absorbance bands (from 522 and 558 nm to 533 and 568 nm respectively) for ion-associates in solution. These bands are characteristic for fluorescent part of dye molecule (rigidly connected aromatic rings) and it points to strong interaction between this molecule part and POM surface. Furthermore, this interaction leads to very effective fluorescence resonance energy transfer (FRIP) from RhB molecules (donor) to nanocluster Mo₁₃₈ (acceptor) by both radiative and non-radiative ways. That was confirmed by the reduction of luminescence intensity (at 592 nm) in \sim 100 times. Moreover, the excitation in the POM absorbance band at 750 nm, which corresponds to the presence of Mo^V centers in POM structure, does not show the reversible energy transfer from POM to RhB. It is very important to effective promotion of the potential catalytic activities of POM Mo₁₃₈ conditioned by the presence of molybdenum in variable valency. The analysis of the Raman-spectra of pure RhB and produced ion associates revealed the differences of the xanthene conjugated aromatic system behavior at excitation by the laser with wavelength 488 nm. Thus new supramolecular system with the nonreversible resonance energy transfer possesses the potential ability to use for light-controlled catalysis.