Compounds and metalopolymers with the cluster core [Mo$_6$Cl$_8$]$^{4+}$ and their emissive properties

O.A. Adamenko[1], G.V. Loukova[1]*, V.V. Smirnov[1],
S.E. Starodubova[1,2] and I.E. Uflyand[2]
[1] Institute of Problems of Chemical Physics
Russian Academy of Sciences
142432 Chernogolovka, Moscow Region, Russia
[2] Rostov State Pedagogical University
344082 Rostov-on-Don, Bolshaya Sadovaya St., 33
Fax: c. E-mail: gloukova@cat.icp.ac.ru

Most recent research efforts were devoted to obtaining materials incorporating transition-metal nanoclusters (1–10 nm) owing to the known and possible use in optics, electronics, and catalysis. Notably, one of most significant problems related to the polymer design is phase separation and aggregation of monodisperse clusters within a polymer matrix. In this connection, metal-containing monomers with unsaturated terminal groups, capable of further polymerising, are of special interest.

We have succeeded in obtaining Mo^{II}-cluster-based compounds consisting of the substitution resistant core [Mo$_6$Cl$_8{}^i$]$^{4+}$.[1–3] The cluster core [Mo$_6$Cl$_8{}^i$]$^{4+}$ is a known structural motif; it consists of six molybdenum atoms in an octahedral arrangement with eight face-bridging inner ligands (chlorides, labelled *i*) and six semilabile terminal outer ligands (labelled *o*). The successive replacement of six outer-sphere ligands with other appropriate semilabile ligands (note the core is preserved) is known to facilitate the preparative chemistry of the promising clusters [Mo$_6$Cl$_8{}^i$L$_6{}^o$]$^{2–}$. Herein, we report the preparation and characterisation of novel Mo(II) cluster compounds having easily replaceable ligands Cl$^–$ and CF$_3$COO$^–$ and the ligands CH$_2$=CHCOO$^–$, allowing further radical copolymerisation of the cluster compounds.

We studied photophysical properties (absorption and luminescence) of the cluster salts $(Bu_4N)_2[(Mo^{II}{}_6Cl_8)L_6]$ (where L= CF$_3$COO$^–$, CH$_2$=CHCOO$^–$) and the copolymers $(Bu_4N)_2[(Mo^{II}{}_6Cl_8)(CF_3COO)_{6–n}]$–polyacrylic acid. The cluster-containing monomers and corresponding copolymers were shown to intensely emit (τ~0.2–0.4 ms). We assign the observed excited state-to-ground state radiative transition as spin forbidden (phosphorescence: $T_1 \rightarrow S_0$).

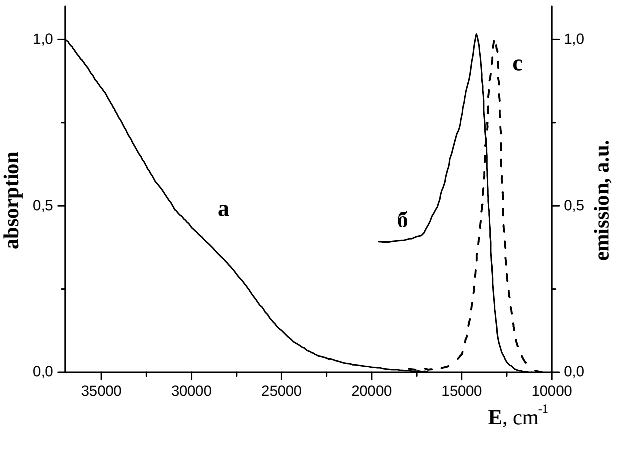

Figure 1. Electronic spectra of absorption of the copolymer solution $(Bu_4N)_2[(Mo_6Cl_8)(CF_3COO)_{6–n}]$-polyacrylic acid in the mixture dioxane + water and at 290 K (***a***) and of luminescence of the solvent-free copolymer at 290 (***b***) and 70 K (***c***) (spectra *b* and *c* were corrected).

Electrochemical studies revealed that cluster dianions undergo reversible oxidation to the corresponding radical anions with apparent preservation of both inner and outer ligand sphere in poorly coordinating solvents (e.g., in CH$_2$Cl$_2$). Alteration of the outer-sphere ligands results in the pronounced change in energy of the highest occupied orbital (HOMO) in the cluster dianions [Mo$_6$Cl$_8{}^i$L$_6{}^o$]$^{2–}$. For a family of Mo$_6$-containing clusters, large contribution from outer-sphere ligands L$_n$ to HOMO of the clusters [(Mo$_6$Cl$_8$)L$_n$]^m was for the first time rationalised on an experimental base. To overall, the electrochemical technique indeed offers possibility to reveal the both predominate preservation of inner- and outer-sphere anionic ligands of a cluster dianion in the course of redox processes and contributions from the outer ligands L^o to frontier orbitals of a cluster dianion (HOMO and LUMO, respectively).

Particular emphasis is given to metalopolymers obtained via radical copolymerisation of the corresponding cluster monomers containing terminal acrylic ligands $(Bu_4N)_2[(Mo_6Cl_8)(CF_3COO)_{n–6}(CH_2{=}CHCOO)_n]$ bearing activated cluster-bound ligands with acrylic acid. Notably, the target cluster-containing copolymers (Mo~1–5 weight %) emit in the region 700–800 nm; the fact also evidences preservation of the cluster core in polymer matrices.

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Reference

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