Letters to the Editor

Rise of photoluminescence in the photolysis of Eu^{III} complexes with copolymers of acrylic acid and butyl methacrylate

A. G. Mirochnik,[a] N. V. Petrochenkova,[a] V. E. Karasev,[a] I. A. Borisov,[a] A. P. Kulikov,[a] and T. Nakajima[b]

[a]*Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences,*
159 prosp. 100-Letiya Vladivostoka, 690022 Vladivostok, Russian Federation.
Fax: +7 (423 2) 31 1889
[b]*National Laboratory of High Energy Physics, Tsukuba, 305 Japan.*
Fax: (0298) 64 2801

The luminescence and photochemical properties of Eu^{III} complexes with copolymers of acrylic acid and butyl methacrylate have been studied by luminescence, IR spectroscopy, and EXAFS.

Key words: europium(III) complexes, copolymers of acrylic acid and butyl methacrylate; luminescence spectra; EXAFS spectra; photolysis.

The mutual effect of macromolecules and rare-earth metal ions involved in a polymeric chain is of considerable interest in fundamental and applied chemistry.[1] In a continuation of our investigations of Eu^{III} complexes with acrylic acid copolymers[2—4] we revealed substantial difference between the photochemical behavior of Eu^{III} complexes with copolymers of acrylic acid and butyl methacrylate and that of their low-molecular analogs and Eu^{III} complexes with polyacrylic acid: during photodecomposition of the metallopolymer the intensity of photoluminescence of Eu^{III} does not decrease, but significantly increases. This is accompanied by changes in the structure of the first coordination sphere of europium.

Synthesis of the copolymer and its complexes with Eu^{III} has been previously described by us.[3] Photolysis of the samples as films on a glass support was carried out by irradiating them with non-filtered light from a DRSh-250 mercury lamp. The distance between the lamp and the sample was 20 cm. The luminescence spectra were recorded with an SDL-1 spectrometer, equipped with a DRSh-250 mercury lamp as a source of excitation and a UFS-6 filter, λ_{max} = 365 nm. The excitation luminescence spectra were obtained with a device based on an SDL-1 spectrometer and an MDR-23 monochromator; a 2500 W Tungsram xenon lamp was used as the source of excitation.

Irradiation of polymeric complexes with UV light results in a decrease in the intensity of the main bands in the IR spectra, and a band appears at 270—280 nm in the electronic absorption spectra. These data attest to photodestruction of the macromolecular ligand. Simultaneously, the intensity of luminescence of Eu^{3+} (electrodipole transition $^5D_0$—$^7F_2$, λ_{lum} = 615 nm) increases 4—25-fold depending on the composition of the macromolecular complex. It is found that a low content

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 958—959, May, 1994.

of acrylic acid in the copolymer and a low concentration of the metal enhance the efficiency of the build-up of Eu^{3+} luminescence under photolysis.

Analysis of the EXAFS spectra of the investigated complexes demonstrated[4] that the first coordination sphere of Eu contains from six to eight O atoms, located at an average distance of 2.47 Å. When the polymeric complexes are photolyzed, the Eu—O interatomic distance increases by 0.15 Å. This increase is accompanied by a decrease in the variation of the Eu—O bond lengths, which is indicated by the reduction of the Debye—Waller factor by 0.001 $Å^{-2}$.

The excitation luminescence spectra of the macromolecular complexes investigated are sets of narrow discrete lines, which correspond to Stark f—f transitions of Eu^{3+}. Their analysis indicates the absence of intramolecular energy transfer from the levels of the macromolecular ligand to the resonance levels of the metal. During UV irradiation of the samples no changes in the structure of the excitation luminescence spectra were revealed, hence the significant increase in the intensity of Eu^{3+} luminescence observed during photolysis cannot be accounted for by an increase in the transfer of electronic excitation energy to Eu^{3+} levels.

It is known that the efficiency of the degradation of the electronic excitation energy on high-frequency vibrations of ligands is one of the factors that affect on the intensity of the luminescence bands of lanthanide ions in complexes.[5] The increase in the Eu—O average distance observed in the photolysis probably favors a decrease in the efficiency of the process of nonradiative dissipation of electronic excitation of Eu^{3+} on high-frequency vibrations of the macromolecular ligand and, therefore, an increase in the intensity of photoluminescence of the ion.

References

1. Y. Okamoto, *J. Macromol. Sci. Chem.*, 1987, **24A**, 455.
2. N. V. Petrochenkova, A. G. Mirochnik, and V. E. Karasev, *Koord. Khim.*, 1991, **17**, 1567 [*Sov. J. Coord. Chem.*, 1991, **17** (Engl. Transl.)].
3. N. V. Petrochenkova, A. G. Mirochnik, and V. E. Karasev, *Koord. Khim.*, 1993, **19**, 166 [*Russ. J. Coord. Chem.*, 1993, **19** (Engl. Transl.)].
4. A. P. Kulikov, A. G. Mirochnik, I. A. Borisov, N. V. Petrochenkova, V. E. Karasev, and T. Nakajima, *Koord. Khim.*, 1992, **18**, 1224 [*Russ. J. Coord. Chem.*, 1992, **18** (Engl. Transl.)].
5. V. L. Ermolaev, E. N. Bodunov, E. B. Sveshnikova, and T. A. Shakhverdov, *Bezyzluchatel'nyi perenos energii elektronnogo vozbuzhdeniya* [*Nonradiative Transition of Energy of Electronic Excitation*], Nauka, Leningrad, 1977 (in Russian).

Received December 21, 1993;
in revised form March 15, 1994

The first optically active organometallic porphyrin: *meso*-tetrakis[(1*S*)-2-methylcymantrenyl]porphine

N. M. Loim, M. A. Kondratenko, E. V. Grishko, and V. I. Sokolov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

It has been shown previously that metallocomplexes of chiral synthetic porphyrins can efficiently catalyze the enantioselective epoxidation of olefins,[1] hydroxylation of alkanes,[2] and oxidation of sulfides.[3] In most cases, the chiral porphyrins used for this purpose have been obtained either by the condensation of pyrrole with an optically active aldehyde or by introducing chiral fragments into molecules of achiral derivatives of *meso*-tetraphenylporphyrins.[4] Literature data on the use of organometallic compounds in the synthesis of chiral porphyrins are lacking.

We synthesized the first optically active organometallic porphyrin by direct condensation of pyrrole with optically active (+)-(1*S*)-2-methylcymantrenecarboxalde-

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 959—961, May, 1994.