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.

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

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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-

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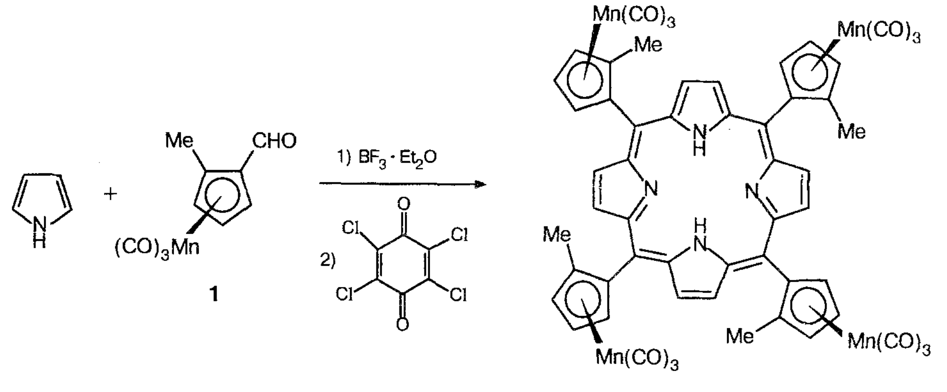

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2

hyde[5] (**1**) in CH_2Cl_2 using $BF_3 \cdot OEt_2$ as the catalyst, *i.e.*, under conditions similar to those reported for the synthesis of *ortho*-substituted tetraphenylporphyrins[6] (the ratio pyrrole : **1** : $BF_3 \cdot OEt_2$ was 1.1 : 1 : 0.1; the reaction was carried out for 20 h under an Ar atmosphere). The oxidation of the intermediate porphyrinogene with *p*-chloroanil (0.8 equiv., 3 h) resulted in *meso*-tetrakis[(1*S*)-2-methylcymantrenyl]porphine (**2**) in 60 % yield. The yield of pure **2** after repeated column chromatography of the reaction products (silica gel, 100—200 μm, benzene—Et_3N (100 : 1)) and reprecipitation from hexane was 47 % (dark-green powder, m.p. >250 °C).

The structure of porphyrin **2** was established by spectral methods and from elemental analysis data. ^1H NMR (toluene-d_8), δ: 10.75, 10.58 and 8.83, 8.55 (all m, 1 H, 3 H, 2 H, and 2 H, H-pyrr.); 5.12, 5.07, 4.98 and 4.46, 4.41 (all m, 4 H and 8 H, H-Cp); 1.79, 1.74×2, 1.70 (all s, 12 H, Me); −1.19, −1.37, −1.48 (all br.s, 2 H, NH). IR (benzene), ν/cm^{-1}: 1938, 2020. UV (CH_2Cl_2), λ_{max}/nm: 372, 448, 506, 545, 582, 622, 678. MS (FAB), *m/z*: 1175 $[M]^+$, 1091 $[M-3CO]^+$. Found (%): C, 58.01; H, 3.54; Mn, 17.87. $C_{56}H_{34}Mn_4N_4O_{12} \cdot {}^1/_2C_6H_{14}$. Calculated (%): C, 58.19; H, 3.39; Mn, 18.05.

The CD spectrum of porphyrin **2** in CH_2Cl_2 displays a number of positive [λ_{max}/nm (Δε): 697 (0.15), 635 (0.2), 612 (0.7), 573 (2.76), 458 (8.82), 427 (3.8), 405 (5.4)] and negative [λ_{max}/nm (Δε): 665 (0.9), 537 (1.47), 510 (0.4), 444 (13.9), 350 (4.3)] Cotton effects in the absorption region of the porphyrin chromophore. Hence, the introduction of chiral cymantrenyl fragments in the porphine molecule renders all electronic transitions of the porphyrin molecule optically active.

Thus, we have found a new way for synthesizing optically active porphyrins based on chiral derivatives of cymantrenecarboxaldehyde that are at present available in the optically active form.[7]

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