Intense luminescence of the Group IVB metal π-complex in solutions at room temperature

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Studies of luminescence, in particular, phosphorescence, are significant in development of the theory of triplet state.[1—3] An important role in photophysics and photochemistry belongs to the solvent, which can also be a reactant and specific quencher of luminescence: the majority of molecules do not luminesce in the liquid phase. Compounds of Group IVB metals[4,5] gained special significance as catalysts of many organic reactions, including olefin polymerization[6—8] and activation of small inert molecules (N_2, CO, CO_2, *etc.*).[9] However, no systematic studies on the interaction of organometallic complexes of early transition metals (in particular, Group IVB metals) with the medium were carried out.

The previous study of the $Cp_2M^{IV}Cl_2$ complexes (Cp = η^5-C_5H_5, M = Ti, Zr, Hf) has revealed[10] their luminescence in solid solutions at low temperature and in polycrystals at low and elevated temperatures. In the present work, we studied for the first time the d^0 metallocene complex based on the Group IVB metal, namely, racemate of *trans*-1,2-[(bis(η^5-tetrahydroindenyl)cyclohexane]zirconium(IV) dichloride, *rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$ (**1**), which intensely luminesces in liquid solutions. The long-lived excited state of complex **1** is formed due to the ligand to metal charge transfer, which is rarely observed in the photophysics of organometallic compounds.[10—12]

Solutions of single crystals were studied. All solvents used were multiply purified from traces of impurities, oxygen, and moisture and subjected to freezing—thawing out cycles using known procedures.[10—12] The concentration of the complex in solutions was 10^{-5}—10^{-4} mol L^{-1}. Spectral measurements were conducted by an earlier described procedure.[13]

Complex **1** luminesces in the liquid phase at room temperature (the luminescence lifetime in hydrocarbon media is ~2 ms at 77 K). The absorption and luminescence spectra of complex **1** at 20 °C in acetonitrile and methylcyclohexane are shown in Fig. 1. It can be seen that an increase in the polarity of the solvent results in the red shift of the absorption spectra and (to a greater extent) luminescence spectra: up to 1000 cm^{-1} and more. The quantum yields (Φ) of luminescence of solutions presented in Fig. 2 (to Φ ~30% in dichloromethane) are

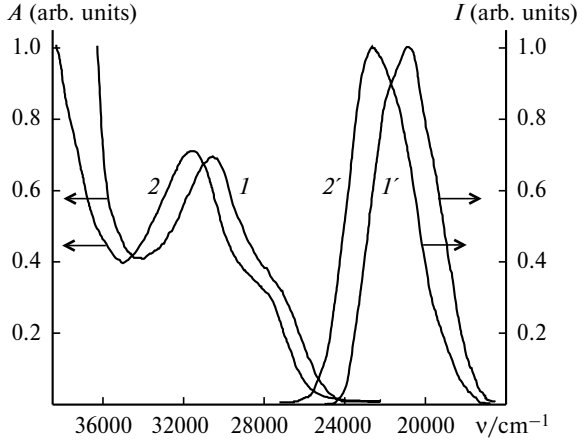

Fig. 1. Absorption (*A*) (*1*, *2*) and luminescence (*I*) (*1′*, *2′*) spectra of complex **1** at 20 °C in acetonitrile (*1*, *1′*) and methylcyclohexane (*2*, *2′*) (luminescence spectra are normalized; λ_{exc} = 350 nm).

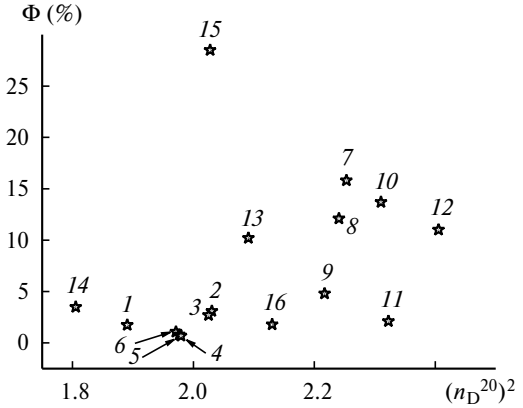

Fig. 2. Quantum yields of luminescence of complex **1** at 20 °C in hexane (*1*), cyclohexane (*2*), methylcyclohexane (*3*), tetrahydrofuran (*4*), 2-methyltetrahydrofuran (*5*), 2,5-dimethyltetrahydrofuran (*6*), benzene (*7*), toluene (*8*), *sec*-butylbenzene (*9*), 4-chlorotoluene (*10*), chlorobenzene (*11*), 1,2-dichlorobenzene (*12*), chloroform (*13*), acetonitrile (*14*), dichloromethane (*15*), and tetrachloromethane (*16*); $(n_D^{20})^2$ is the optical dielectric constant.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 171—172, January, 2007.

1066-5285/07/5601-0181

among the highest for the known organic and metal-containing molecules and controlled by the nature of specific and, to a lesser extent, universal[14] interactions with solvent molecules. We have shown for the first time that in liquid solutions the triplet state of a metallocene complex of Group IVB metal can be populated as efficiently as in solid media.

The authors are grateful to Prof. A. E. Shilov for helpful discussion and Dr. W. Huhn ("Procter&Gamble Italia," Italy) for kindly presented single-crystal samples of the complex studied.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32792) and the Russian Academy of Sciences (Program of the Division of Chemistry and Materials Science No. 1 "Theoretical and Experimental Investigation of the Chemical Bond Nature and Mechanisms of the Most Important Chemical Reactions" and Program of the Presidium of the RAS No. 8 "Development of Methods for Synthesis of New Chemical Substances and Design of Novel Materials").

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Received May 24, 2006;
in revised form July 10, 2006