Letters to the Editor

Simple correlation between the main luminescence parameters of the metallocene complex in the liquid phase

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Metallocene complexes of Group 4B metals possess rather uncommon phosphorescent states[1—5] appearing due to the ligand to metal charge transfer (LMCT).[1—12] The luminescence quantum yields (Φ_L) and lifetimes of electronically-excited states (τ) of metallocenes of the titanium subgroup are among highest and longest ones for the known LMCT states and other radiative states ($T \rightarrow S_0$) of coordination compounds. In the present work, we studied the lifetimes of the LMCT excited states of metallocene *rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$ (**1**)[13] (Ind is indenyl) in solutions. This metallocene intensely luminesces in the liquid state at room temperature. The proportional dependence $\Phi_L \propto \tau$ of the radiative characteristics of compound **1** was observed in solvents of different solvating ability.

Solutions prepared from single crystals of compound **1** were studied. All solvents were subjected to special repetitive purification from traces of admixtures, oxygen, and moisture using freezing—thawing out cycles in a high-vacuum line according to known procedures.[1—4] The concentration of the complex in solutions was $3 \cdot 10^{-5}$—$2 \cdot 10^{-4}$ mol L^{-1}. The lifetimes were determined upon the excitation of solutions of metallocene **1** by a photodiode laser with λ_{exc} = 375 nm on a Fluotime 200 fluorimeter (PicoQuant GmbH, Germany) using the photon counting method and the commercial FluoFit program package. The luminescence quantum yields of solutions of compound **1** were determined by a comparison of the integral luminescence intensities of the sample (D_x) and standard solution (D_{st}) with a correction for the difference of the refractive coefficients of the solvent in the sample (n_x) and in the standard (n_{st}) using the known formula

$$\Phi_{L,x}/\Phi_{L,st} = (n_x^2/n_{st}^2)(D_x/D_{st}).$$

An anthracene solution in ethanol ($\Phi_{L,st}$ = 0.27) was used as standard.[14] The accuracy of determination of Φ_L was at least ±10%.

We obtained a linear correlation for the main emission parameters

$$\Phi_L = k_r\tau,$$

where k_r is the radiative deactivation constant for the excited state (for solutions of **1** $k_r = 2.36 \cdot 10^4$ s^{-1}; Fig. 1), which was observed for the first time for the luminescence of all known molecules in solutions. The solvent determines the nonradiative deactivation rate (k_{nr}) rather than k_r, which is expressed as the relation $\Phi_L \propto \tau$. Note that the Φ_L and τ parameters strongly depend nonlinearly on the medium effects, most probably, because of specific

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2272—2274, November, 2007.

1066-5285/07/5611-2351

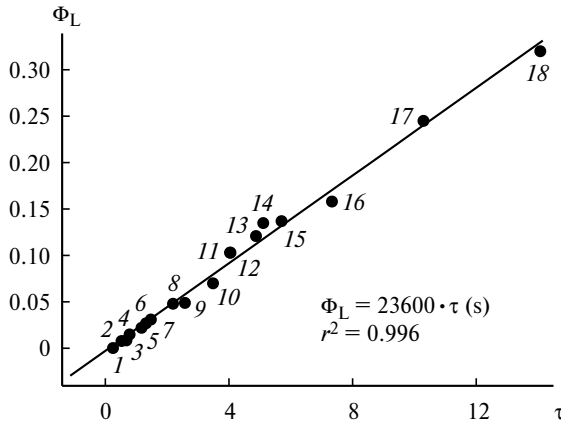

Fig. 1. Linear relation of the luminescence quantum yield (Φ_L) and the lifetime of the LMCT state (τ) of metallocene **1** in bromotrichloromethane (*1*), hex-1-ene (*2*), 2-methyltetrahydrofuran (*3*), pentane (*4*), tetrachloromethane (*5*), methylcyclohexane (*6*), cyclohexane (*7*), butylbenzene (*8*), acetonitrile (*9*), *p*-xylene (*10*), ethylbenzene (*11*), *m*-xylene (*12*), toluene (*13*), *o*-xylene (*14*), *p*-chlorotoluene (*15*), benzene (*16*), 1,2-dichloroethane (*17*), and dichloromethane (*18*) at 20 °C.

interactions of the complex with aprotic solvents of different nature. This dependence cannot be explained by one simple regularity (for instance, by the dependence on the dielectric constant ε or n_D^2). We believe that the main factors determining the quantum yield and lifetime of the radiative state of d^0-metallocene in solution are the strong solvation (*via* the mechanism of outer-sphere coordination of molecules of the medium) and the absence of inner-sphere coordination of the solvent by the solute (for example, where quenching can occur *via* the exciplex mechanism). Quite strong donor—acceptor interaction is also observed when 2-methyltetrahydrofuran was used as solvent. In this case, the donor—acceptor σ-bond is formed due to a lone electron pair of the O atom (ether) and the vacant orbital of Zr^{4+} (in this case, Φ_L and τ are low). We exclude the influence of the HOMO—LUMO* energy gap (determined as the energy of the 0—0-transition (E_{00}) or the energy of the luminescence maximum (E_{max})) on the Φ_L and τ parameters: the range, in which the gap values for complex **1** are varied in the series of solvents, is too narrow (E_{00} = 2.94—3.11 eV and E_{max} = 2.58—2.81 eV, *i.e.*, ΔE = 5—8% of the gap value) to expect considerable changes in Φ_L and τ. In our opinion, the strong outer-sphere solvation makes the structure of the complex more rigid ("rigid matrix effect"), which decreases the probability of nonradiative deactivation due to vibrational relaxation and bimolecular quenching in solution. The efficiency of solvation depends on the macroscopic parameters of the solvent (ε, n_D^2) and the specific (coordination, chemical) interaction with the solute.

The data presented in Fig. 1 indicate that the radiative characteristics Φ_L and τ are very sensitive to the properties and structure of the medium molecules (see, *e.g.*, the series pentane—cyclohexane—methylcyclohexane, alkylbenzenes, isomeric xylenes) and can be used when studying intermolecular interactions in highly organized (for example, catalytic) systems based on metallocenes of Group 4B metals. In our case, the specificity of the interaction is manifested as a monotonic decrease in the luminescence quantum yield and lifetime with the enhancement of steric hindrance in the C_6 ring of the solvent molecules. Such systematically modified hindrances are, for instance, the alkyl substituent length in alkylbenzenes and the position of substituents in the xylene isomers. For example, at virtually identical macroscopic properties (ε, n_D^2, influence on E_{00} and E_{max}), as in the case of alkyl-substituted benzenes, a strong medium effect on the luminescence characteristics Φ_L and τ was observed.

Thus, in the present work, we revealed that the main luminescence characteristics (Φ_L and τ) of solutions of complex **1** depend strongly on the solvent nature; the long lifetimes and high luminescence quantum yields are observed in media with a stronger solvating ability toward the metallocene complexes. The solvent determines the nonradiative deactivation rate, which is expressed as the linear relation between the Φ_L and τ parameters.

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

This work was financially supported by 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 Chemical Substances and Design of Novel Materials").

* The so-called "energy gap law" [15—19], which is expressed as the linear increase in $\ln(k_{nr})$ with a decrease in the emission energy E_{max}, is known for a series of metal complexes, including the half-sandwich d^0-complexes of Group 5B metals.[20]

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Received February 19, 2007;
in revised form August 21, 2007