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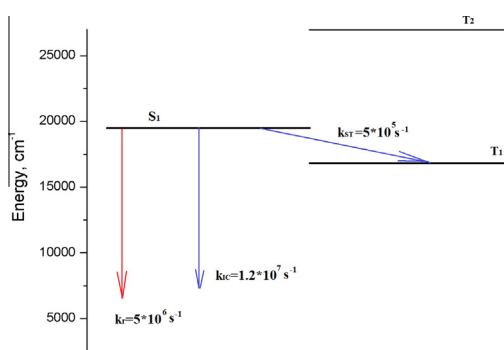
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journal homepage: www.elsevier.com/locate/saaTheoretical and experimental investigation of photophysical properties of Zn(DFP SAMQ)₂R.R. Valiev^{a,b,*}, E.N. Telminov^a, T.A. Solodova^a, E.N. Ponyavina^a, R.M. Gadirov^a, M.G. Kaplunov^c, T.N. Kopylova^a^a Tomsk State University, 36 Lenin Avenue, Tomsk 634050, Russia^b Tomsk Polytechnic University, 43a Lenin Avenue, Building 2, Tomsk 634050, Russia^c Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

HIGHLIGHTS

- The photophysical properties of Zn(DFP SAMQ)₂ were investigated.
- The matrix element of spin–orbital coupling operator was computed.
- The rate constants of radiationless electronic transitions were estimated.

GRAPHICAL ABSTRACT



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ABSTRACT

Theoretical calculations and experimental measurements were carried out for the investigation of spectroscopic and photophysical properties of Zn(DFP SAMQ)₂ complex. The rate constant of intersystem crossing and the radiative rate constant were calculated using *ab initio* method. The rate constant of the internal conversion was estimated using the received calculated values and the experimental fluorescence quantum yield. It was shown that the main mechanism for the deactivation of the excited electronic energy of the first singlet excited state is the process of internal conversion.

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Introduction

Organometallic compounds are widely used in the creation of devices of organic and quantum electronics due to high quantum efficiency [1–5]. It should be noted, that the most of zinc

complexes have the electroluminescence properties and, thus, they are used in design of organic light-emitting diodes (OLED) [6]. This is the reason of the search of electro-luminophores in this class of compounds [6–9]. Note that the electrons of zinc are not involved in $\pi\pi^*$ -transitions in zinc complexes and so the electronic spectra of zinc complexes are just the spectra of free ligands [10]. However, the ions of zinc play the coordinative role in the compounds. Therefore, the investigation of structural and photophysical properties of organometallic compounds is required at the first steps of the designing devices.

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It is well known that the investigation of photophysical properties of molecules is concerned with the estimation of probabilities of the deactivation of electronic excited energy through different channels of relaxation [11–20]. The most important photophysical processes are intramolecular deactivation processes of electronic excited energy. They are the emission, the internal conversion and the intersystem crossing.

At present time, the calculation of rate constant of intersystem crossing (k_{ST}) can be performed using quantum chemical software's [17–20]. However, the computation of rate constant of internal conversion (k_{IC}) is not a trivial procedure [17–22]. The estimation of the value of k_{IC} is impossible for large molecules with methods of quantum chemistry. Thus, both theoretical and experimental methods are required for the investigation of photophysical properties of molecules.

Recently, new zinc complexes were synthesized [23]. They have a significant electroluminescence. The most perspective compound among them is bis-[8-(3,5,5-difluorophenyl)sulfanillamine]quinoline zinc complex ($\text{Zn}(\text{DFP SAMQ})_2$) due to sizable fluorescence quantum yield (0.3) [23]. In the works of Kaplunov et al., the electroluminescence properties of the considered compound were measured [23]. Also, in the work of Minaev et al., the equilibrium geometry of electronic ground state (S_0) and vertical electronic excited states energies for the considered complex were calculated using density function level of theory [10,24]. However, the reliable theoretical results can be computed using *ab initio* wave function-based methods. It should be noted also, that theoretical investigation of photophysical properties of $\text{Zn}(\text{DFP SAMQ})_2$ complex has not being carried out. Investigation of radiationless processes of deactivation of the electronic excited energy can give more complete understanding of photophysical properties of zinc complexes and can identify the most promising structures for the use in organic electronics.

The aim of this work is to investigate the spectral and the photophysical properties of $\text{Zn}(\text{DFP SAMQ})_2$ compound for deeper understanding of the photophysical deexcitation processes employing the first-principle calculations and experimental measurements.

Experimental and calculation details

Absorption and luminescence spectra were measured on the SM2203 spectrometer (SOLAR, Belarus). The cyclohexan was used as a solvent for all measurements. The fluorescence quantum yield (QE) was measured taking coumarin-102 as a standard (QE = 0.6) with an error of 10%. The investigation of phosphorescence in frozen solutions (at 77 K) was carried out using the Cary Eclipse spectrofluorimeter with cryostat Optistat DN (Oxford Instruments).

The equilibrium geometries of S_0 and the first excited singlet state (S_1) were optimized using the density function level of theory (DFT) and the time dependent density functional level of theory (TDDFT), respectively. The Becke's three-parameter functional (B3LYP) [25,26] and def2-TZVP basis set [27] were used.

The vertical electronic excited energies and its oscillator strengths were obtained using the extended multi-configurational quasi-degenerate perturbation theory (XMCQDPT2) [28]. Note that 10 electrons in 11 orbitals were included in the active space. State average calculations were performed for the systems under investigation with averaging over 4 states and with the effective Hamiltonian including 30 states. Also, computed wave functions of the S_1 state and the first triplet state T_1 were used in the calculation of the matrix elements of spin–orbital coupling operator between them.

Rate constant k_{ST} was calculated as [29,30]

$$k_{ST} = 10^{10} \cdot \langle \Psi_{S_1} | H_{SO} | \Psi_{T_j} \rangle \cdot F_{on},$$

where $\langle \Psi_{S_1} | H_{SO} | \Psi_{T_j} \rangle$ (in cm^{-1}) is the matrix element of full spin–orbital coupling operator (H_{SO}) between S_1 state and the i -th excited triplet state (T_i), F_{on} – Frank–Condon factor. Here, $10^{10} \text{ cm}^2 \text{ s}^{-1}$ is the fitting parameter. Note that F_{on} was calculated in harmonic approximation with one acceptive mode ($\omega = 1400 \text{ cm}^{-1}$) [30]. The $\langle \Psi_{S_1} | H_{SO} | \Psi_{T_j} \rangle$ were calculated using the multi-configurational self-consistent field (MCSCF) with def2-TZVP basis set and 10 electrons in 11 orbitals in active space.

The radiative rate constant (k_r) was calculated according to the formula:

$$k_r = \frac{1}{1.5003} \cdot f \cdot E^2$$

where f is oscillator strength and E is the energy (in cm^{-1}) of the $S_1 \rightarrow S_0$ vertical electronic transition.

All calculations were performed using software packages Firefly [31] and Gamess-US [32].

Results and discussions

Molecular structure

The equilibrium structure of S_1 state is given in Fig. 1. The Cartesian coordinates of atoms in the equilibrium geometries of S_1 and S_0 are given in supplementary material. Note that only the lengths of bonds of chinolin group and N2–Zn bond are significantly changed during the transition from S_0 to S_1 states (Table 1) and other bond lengths stayed the same.

Spectroscopic properties

The measured electronic absorption and fluorescence spectra are shown in Fig. 2. As seen from the figure, the first and the second bands have maximum intensity at 371 nm and 322 nm, respectively. The fluorescence is observed at 500 nm. The Stokes shift equals to 130 nm ($\sim 7000 \text{ cm}^{-1}$). The large value of Stokes shift can be explained by significant change of the bond lengths (mainly chinolin group) at excitation (Table 1).

The results of theoretical calculations of energies of the vertical excited electronic states and its oscillator strengths and the contributions of the most relevant configuration state functions are given in Table 2. The comparison of the measured electronic absorption spectra with calculated characteristics of the electronic transitions shows, that the first absorption band is formed by $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transitions and the second band is formed by $S_0 \rightarrow S_3$ one. Also, according to Table 2, the S_1 state is formed mainly by the electronic transition from HOMO to LUMO. Besides,

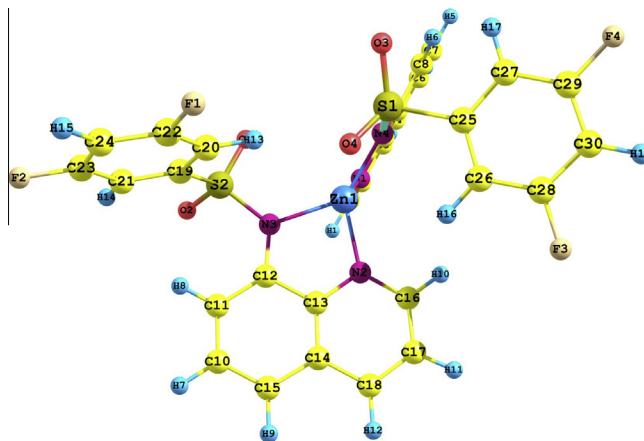
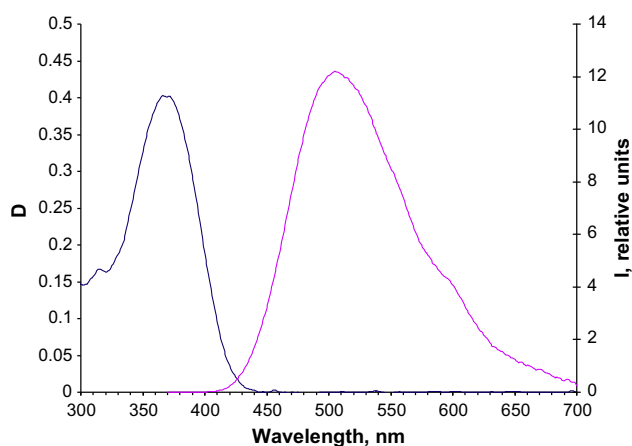


Fig. 1. Equilibrium structure of the $\text{Zn}(\text{DFP SAMQ})_2$ molecule in the S_1 state.

Table 1The bond lengths (in Angstroms) for S_0 and S_1 states of $\text{Zn}(\text{DFP SAMQ})_2$.

The bond	S_0 state	S_1 state
C10–C11	1.415	1.393
C11–C12	1.394	1.426
C13–C14	1.428	1.389
C14–C15	1.420	1.437
C14–C18	1.419	1.445
C17–C18	1.381	1.406
C16–C17	1.411	1.384
C13–N2	1.370	1.392
C16–N2	1.327	1.384
N2–Zn1	2.132	1.989
C12–N3	1.388	1.357

**Fig. 2.** Electronic absorption spectrum (brown curve) and fluorescence spectrum (red curve) of $\text{Zn}(\text{DFP SAMQ})_2$ compound. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the Fig. 3 shows that HOMO and LUMO are located on chinolin group. This fact completely explains the large value of Stokes shift of $\text{Zn}(\text{DFP SAMQ})_2$ because the bond lengths of chinolin group are significantly changed at excitation. It should be noted, in the work of Minaev et al. the closely location of S_1 and S_2 states were explained by the quasi-degeneracy nature of HOMO, HOMO-1, LUMO and LUMO + 1 orbitals [10,24]

Photophysical properties

In this work, the experimental investigation shows that there is a short-lived emission (Fig. 1) and not the long-lived emission for $\text{Zn}(\text{DFP SAMQ})_2$ compound. Also, the measured fluorescence quantum yield is 0.3. The triplet excited states and the energy of $S_1 \rightarrow S_0$ electronic transition in the equilibrium geometry of S_1 state were calculated in order to explain the absence of phosphorescence and the investigation of the radiationless relaxation processes of electronic excited energy (Table 3). As seen from Table 3, only one triplet state (T_1) is lower than the S_1 state. Therefore, the S_1 energy can be deactivated by the internal conversion ($S_1 \rightarrow S_0$), the intersystem crossing ($S_1 \rightarrow T_1$) and by the photon emission (the radiative electronic transition) (Fig. 4).

The calculated matrix element of the spin–orbital coupling operator $\langle \Psi_{S_1} | H_{SO} | \Psi_{T_1} \rangle$, the k_{ST} between S_1 and T_1 states and the k_r from S_1 to S_0 states for $\text{Zn}(\text{DFP SAMQ})_2$ are given in Table 4. As seen from the table the value of $\langle \Psi_{S_1} | H_{SO} | \Psi_{T_1} \rangle$ is very small. As a result, the value of k_{ST} is one order of magnitude less than the value of k_r . Note, that k_{IC} can be estimated using the experimental value of fluorescence quantum yield $\phi_f = 0.3$, the calculated values of k_{ST} , k_r and the following formula [30]:

$$\phi_f = \frac{k_r}{k_r + k_{IC} + k_{S_1T_1}}$$

The estimation of k_{IC} leads to $1.2 \times 10^7 \text{ s}^{-1}$ (Fig. 4). Therefore, the process of internal conversion dominates in the fluorescence

Table 2

Contributions of the most relevant configuration state functions (the weights are given in parenthesis) of complete active space self consistent field (CASSCF) calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E , in cm^{-1}) and oscillator strengths (f) for the first three electronic excited states of $\text{Zn}(\text{DFP SAMQ})_2$ compound.

Electronic transition	Configuration	Energy (f)	Experiment
$S_0 \rightarrow S_1$	HOMO \rightarrow LUMO (0.63)	XMCQDPT2 24,090 (0.10)	
$S_0 \rightarrow S_2$	HOMO-1 \rightarrow LUMO + 1 (0.59)	26,580 (0.09)	27,020 (0.12)
$S_0 \rightarrow S_3$	HOMO \rightarrow LUMO + 3 (-0.44)		
	HOMO-4 \rightarrow LUMO (-0.34)	30,943 (0.01)	31,700 (0.03)
	HOMO \rightarrow LUMO + 5 (0.23)		

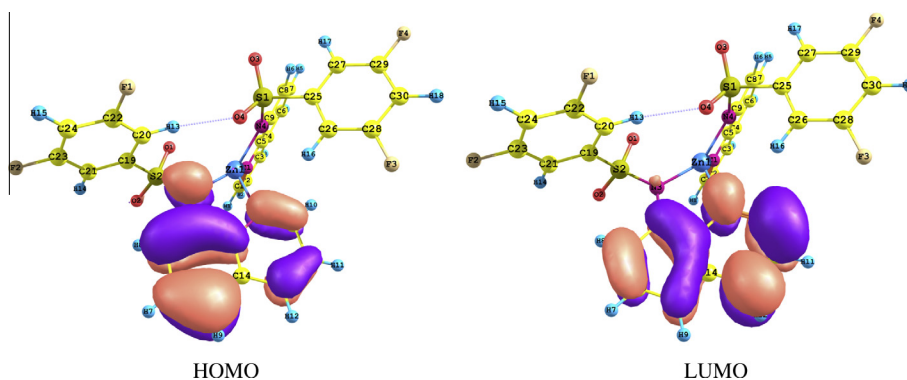
**Fig. 3.** Scheme of the HOMO and LUMO molecular orbitals.

Table 3

The XMCQDPT2 calculated and experimental electronic excitation energies (E in cm^{-1}) and their oscillator strengths of $\text{Zn}(\text{DFP SAMQ})_2$ compound.

Transition	$E(f)$ (cm^{-1})	Experiment (cm^{-1})
$S_1 \rightarrow S_0$	19,500 (0.02)	20,000
T_1	16,800	
T_2	21,400	
T_3	26,000	

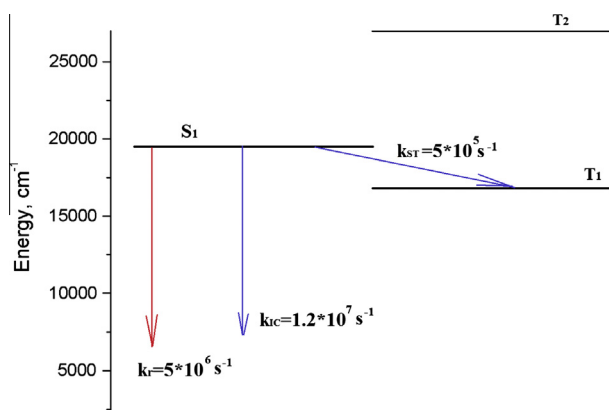


Fig. 4. The calculated energy levels and rate constants for the photophysical processes of $\text{Zn}(\text{DFP SAMQ})_2$ compound. The red arrow and the blue arrows illustrate the radiation and the radiationless deactivation processes, respectively (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Table 4

Computed spin-orbit coupling matrix elements H_{SO} , k_{ST} and k_r for $\text{Zn}(\text{DFP SAMQ})_2$ compound.

$\langle \Psi_{S_1} H_{SO} \Psi_{S_1} \rangle$ (cm^{-1})	k_{ST} (s^{-1})	k_r (s^{-1})
0.05	5×10^5	5×10^6

quenching. Also, the results of Table 4 explain the absence of phosphorescence processes for $\text{Zn}(\text{DFP SAMQ})_2$. The population of T_1 state is not sufficient for the occurrence of phosphorescence because the value of k_{ST} is significantly small in comparison with values of k_{IC} and k_{ST} . Thus, it can be assumed that the nature of electroluminescence emission is fluorescence.

Conclusion

The complex method, based on theoretical calculations and experimental measurements, was carried out for the investigation of the photophysical properties of $\text{Zn}(\text{DFP SAMQ})_2$ compound. As a

result, it was shown that zinc weakly influences on the values of the matrix elements of spin–orbit coupling operator and plays only the coordinative role. Also, the main mechanism for the deactivation of the excited electronic energy of S_1 state is the internal conversion. Therefore the phosphorescence is absent for considered complex and the nature of electroluminescence is the process of fluorescence.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2014.02.157>.

References

- [1] J. Kido, Y. Okamoto, *Organo Lanthanide*, Chem. Rev. 102 (2002) 2357.
- [2] J.A.G. Williams, S. Develay, D.L. Rochester, L. Murphy, *Coord. Chem. Rev.* 252 (2008) 2596.
- [3] L. Lepneva, A. Vaschenko, A. Vitukhnovsky, S. Eliseeva, O. Kotova, N. Kuzmina, *Syn. Metals* 159 (2009) 625.
- [4] P.A. Vigato, S. Tamburini, *Coord. Chem. Rev.* 248 (2004) 1717.
- [5] K.C. Gupta, A.K. Sutar, *Coord. Chem. Rev.* 252 (2008) 1420.
- [6] B. Minaev, G. Baryshnikov, H. Agren, *Phys. Chem. Chem. Phys.* 16 (2014) 1719.
- [7] J. Hoa, C.-Y. Chen, *J. Electrochem. Soc.* 152 (2005) 57.
- [8] R.D. Costa, E. Orti, H.J. Bolink, F. Monti, G. Accorsi, N. Armadori, *Angew. Chem. Int. Ed.* 51 (2012) 8178.
- [9] G.V. Baryshnikov, B.F. Minaev, A.A. Korop, V.A. Minaeva, A.N. Gusev, *Russ. J. Inorg. Chem.* 58 (2013) 928.
- [10] B.F. Minaev, G.V. Baryshnikov, A.A. Korop, V.A. Minaeva, M.G. Kaplunov, *Opt. Spectrosc.* 114 (2013) 30.
- [11] R. Valiev, E. Ermolina, Y. Kalugina, R. Kuznetsova, V. Cherepanov, *Spectrochim. Acta A* 87 (2012) 40.
- [12] B. Minaev, *Spectrochim. Acta A* 60 (2002) 3213.
- [13] O. Loboda, I. Tunell, B. Minaev, H. Agren, *Chem. Phys. Lett.* 312 (2005) 299.
- [14] B.F. Minaev, A.B. Minaev, *Opt. Spectrosc.* 98 (2005) 214.
- [15] B. Minaev, E. Jansson, H. Agren, *J. Chem. Phys.* 125 (2006) 234704.
- [16] S. Perun, J. Tatchen, C.M. Marian, *Chem. Phys. Chem.* 9 (2008) 282.
- [17] C. Marian, *WIREs Rev. Comp. Molec. Sci.* 2 (2012) 187.
- [18] G. Hirsch, P.J. Bruna, R.J. Buenker, S.D. Peyerimhoff, *Chem. Phys. Lett.* 45 (1980) 335.
- [19] V.G. Plotnikov, V.A. Dolgikh, V.M. Komarov, *Opt. Spectrosc.* 43 (1977) 522.
- [20] V.G. Plotnikov, *Intern. J. Quantum Chem.* 16 (1979) 527.
- [21] S.P. McGlynn, T. Azumi, M. Kinoshita, *Molecular Spectroscopy of the Triplet State*, Englewood Cliffs, New Jersey, 1969. p. 28.
- [22] D. Dolphin, *The Porphyrins*, Academic Press, New York, 1978.
- [23] M.G. Kaplunov, I.K. Yakushchenko, S.S. Krasnikova, A.P. Pivovarov, I.O. Balashova, *High Energy Chem.* 42 (2008) 563.
- [24] B.F. Minaev, G.V. Baryshnikov, A.A. Korop, V.A. Minaeva, M.G. Kaplunov, *Opt. Spectrosc.* 113 (2012) 298.
- [25] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [26] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [27] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 7 (2005) 3297.
- [28] A.A. Granovsky, *J. Chem. Phys.* 134 (2011) 214113.
- [29] D.G. Fedorov, S. Koseki, M.W. Schmidt, M.S. Gordon, *Int. Rev. Phys. Chem.* 22 (2003) 551.
- [30] R.R. Valiev, V.N. Cherepanov, V. Ya. Artyukhov, Dage Sundholm, *Phys. Chem. Chem. Phys.* 14 (2012) 11508.
- [31] Firefly, Alex A. Granovsky, Firefly version 8.0.0, <<http://www.classic.chem.msu.su/gran/firefly/index.html>>.
- [32] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* 14 (1993) 1347.