



TIME-DEPENDENT DENSITY FUNCTIONAL THEORY STUDY OF THE LUMINESCENCE OF 2-AMINOPYRIMIDINE DERIVATIVE

N. A. Shekhovtsov^{1,2}, K. A. Vinogradova^{1,2}, M. B. Bushuev^{1,2}

¹Novosibirsk State University, 630090, Russia, Novosibirsk, Pirogova str., 2, shna1998@mail.ru

²Nikolaev Institute of Inorganic Chemistry, 630090, Russia, Novosibirsk, Akad. Lavrentiev Ave., 3

Introduction:

Excited state proton transfer (ESPT) is one of the most important and most studied photoreactions in organic chemistry and photochemistry [1]. Compounds comprising proton donor and acceptor groups linked by short intra- or intermolecular hydrogen bonds favor the ESPT process. One of the most useful consequences of such phototautomerization in ESPT compounds is their dual excitation wavelength dependent fluorescence: the high-energy emission band originates from the “normal” form while the low-energy emission band arises from a phototautomer formed as a result of the ESPT process (Fig. 1). Compared to the excited state proton transfer, excited state double proton transfer (ESDPT) is a rather rare phenomenon which occurs in a limited group of compounds. Pyridine and pyrimidine derivatives were shown to manifest intermolecular ESDPT process in the solid state.

Recently our group reported dual excitation wavelength dependent fluorescence of 2-amino-4-methylpyrimidine (**L**) [2]. In this context we decided to perform theoretical calculations of 2-amino-4-methylpyrimidine using density functional theory (DFT) and compare the results to the experimental data. The goals of our calculations are (i) to confirm the possibility of excited state double proton transfer and (ii) to determine the nature of electronic transitions for both emission bands in the emission spectra of 2-amino-4-methylpyrimidine.

Quantum chemical calculations:

To analyze the electronic structures of a monomer **L** and a hydrogen-bonded dimer **L₂**, quantum chemical calculations were performed using a density functional theory (DFT) approach with the three-parameter hybrid functional B3LYP for geometry optimizations and time dependent DFT calculations (TD-DFT). The D95V basis set and Gaussian 09 code was used in all calculations.

Results and discussion:

The high-energy emission band of **L** at 350 nm (Fig. 2) is associated with the fluorescence of the monomeric form of **L**. TD-DFT computations reveal that S₁-S₀ emission energy is equivalent to 377 nm. This value is only 27 nm higher compared to the experimental maximum of the high-energy emission band (350 nm). The S₁-S₀ emission for the monomer **L** is purely HOMO – LUMO transition. The HOMO is localized on the aromatic π-system and on the lone pairs of two nitrogen

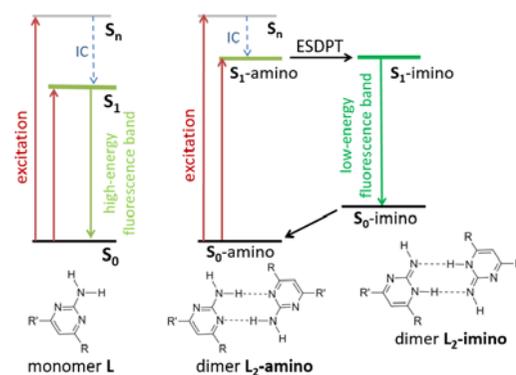


Fig. 1. A simplified energy level diagram showing typical photophysical properties of pyrimidine derivatives in the solid state.

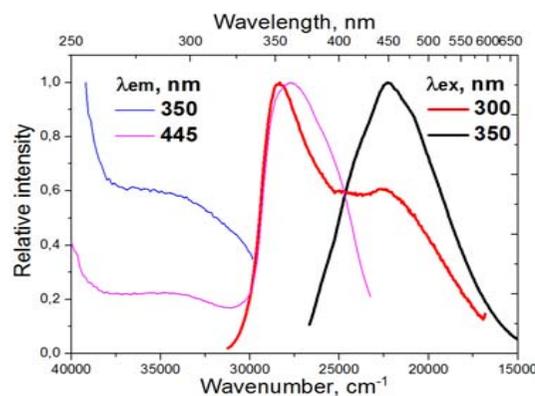


Fig. 2. Excitation ($\lambda_{em} = 350$ and 445 nm) and emission ($\lambda_{ex} = 300$ and 350 nm) spectra of **L**.

atoms, whereas the LUMO is localized mainly on the aromatic π-system. Thus, the high-energy emission band has mixed π-π*, n-π* character.

The low-energy emission band at 445 nm (Fig. 2) can be related to the fluorescence of a tautomeric dimeric associate formed as a result of ESDPT process. This assumption is qualitatively confirmed by the calculated S₁-S₀ emission energies. According to our TD-DFT calculations, the S₁-S₀ transition of the **L₂-imino** associate (595 nm) is notably redshifted as compared to the S₁-S₀ transition of the **L₂-amino** associate (322 nm). Therefore, the S₁-S₀ relaxation of the **L₂-imino** associate causes the low-energy emission band of **L** in the solid state. The frontier molecular orbitals involved in the S₁-S₀ transition of **L₂-imino** (Fig. 3) reveal that it has mixed π-π*, n-π* character.

To gain an insight into the phenomenon of excited state double proton transfer, the potential energy of the dimers **L₂** as a function of the proton transfer reaction coordinate has been calculated by TD-DFT method (Fig. 4). We have optimized the structures of the dimeric associates in the ground state (S₀) and in the first excited singlet state (S₁) keeping the N₁-H₁ and N₂-H₂ bond lengths between 0.8 to 2.2 Å. The energy curve of the first excited singlet state (S₁) was obtained by the vertical transition of each ground state optimized geometry followed by optimization of the excited state using TD-DFT calculations. There are two minima both in the ground state and in the first excited singlet state corresponding to **L₂-amino** (R_{N₁-H₁} = R_{N₂-H₂} = 1.0 Å) and **L₂-imino** (R_{N₁-H₁} = R_{N₂-H₂} = 2.0 Å) forms. The excited state energy barrier (177 kJ/mol) and the ground state energy barrier (218 kJ/mol) are energetically high. Thus, we suppose that the tautomerization process is governed by proton tunneling.

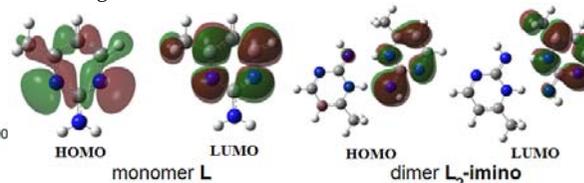


Fig. 3. Iso-surface contour of the frontier molecular orbitals.

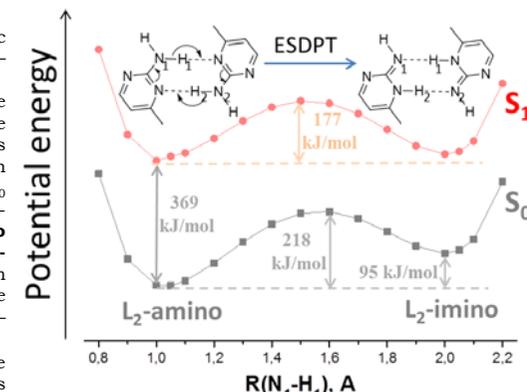


Fig. 4. 2D potential energy curves for the ground and first singlet excited states of **L₂** with variation of N₁-H₁ and N₂-H₂ bond lengths.

Conclusion:

DFT calculations let us reveal relaxation pathways for both fluorescence bands of **L**. The high-energy emission band in the photoluminescence spectrum of **L** originates from the monomer while the low-energy emission band probably arises from a hydrogen-bonded phototautomer. TD-DFT calculated 2D potential energy curves along proton transfer reaction indicate the presence of two stable forms - **L₂-amino** and **L₂-imino**.

Acknowledgements:

The reported research was funded by Russian Foundation for Basic Research and the government of the Novosibirsk region of the Russian Federation, grant No 18-43-540016 r_a.

References:

1. P. Zhou, K. Han. *Acc. Chem. Res.*, **2018**, 51, 1681.
2. K. A. Vinogradova, N. A. Shekhovtsov, A. S. Berezin, T. S. Sukhikh, V. P. Krivopalov, E. B. Nikolaenkova, I. V. Plokhikh, M. B. Bushuev. *Inorg. Chem. Comm.*, **2019**, 100, 11.