

References

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

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

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

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

Keywords: fluorescence, pyrimidine, TD-DFT calculations, excited state double proton transfer, excitation wavelength dependent emission.

The excitation wavelength dependent photoluminescence property has aroused great research interest due to its potential applications in sensors, optoelectronic devices, biological labelling and information encryption [1–3]. Dual fluorescence behavior in the solid state depending on excitation energy is typical for pyridine and pyrimidine derivatives [4–5]. High-energy emission band is ascribed to the fluorescence of a monomeric molecule while low-energy emission band is related to the fluorescence of a tautomeric dimeric associate formed as a result of excited state double proton transfer (ESDPT) process (fig. 1). In the last case two protons are shifted from the amino groups to aza-atoms of the pyrimidine ring in the $\{N-H\cdots N\}_2$ hydrogen bonding synthon.

Recently our group reported dual excitation wavelength dependent fluorescence in 2-amino-4-methylpyrimidine (L, fig. 1) [6]. To gain insight into the phenomenon of

dual fluorescence in L, we decided to perform theoretical calculations using time-dependent density functional theory (TD-DFT). Calculated S_1 – S_0 emission energy for S_1 optimized geometry of the monomer L is equivalent to 353 nm. This value is only 3 nm higher compared to the experimental maximum of the high-energy emission band (350 nm). Simulated absorption spectra of the monomer L and the hydrogen bonded dimer L_2 were computed at B3LYP/LANL2DZ level of theory and plotted along with the experimental data (fig. 2). The UV-Vis diffuse reflectance spectrum of L in the solid state in the region of 330 – 400 nm agrees with the simulated absorption of the dimer L_2 . The absorption above 330 nm, which is absent in the solution of L in MeCN and in the simulated spectrum of the monomer L, affirms extensive aggregation of the L molecules in the solid state, mainly through N–H···N hydrogen bonds.

The potential energy of the dimers L_2 as a function of the proton transfer reaction coordinate has been calculated by TD-DFT method (fig. 2). We have optimized the structures of the dimeric associates in the ground state (S_0) and in the first excited singlet state (S_1) keeping the N_1 – H_1 and N_2 – H_2 bond lengths between 0.8 to 2.2 Å. There are two minima both in the ground state and in the first excited singlet state corresponding to L_2 -amino ($R_{N_1-H_1} = R_{N_2-H_2} = 1.0$ Å) and L_2 -imino ($R_{N_1-H_1} = R_{N_2-H_2} = 2.0$ Å) forms. The excited state energy barrier (177 kJ/mol) is less than the ground state energy barrier (218 kJ/mol), which favors the ESDPT process in the S_1 state.

Therefore, TD-DFT calculations let us 1) affirm the association of L molecules in the solid state with the formation of $\{N-H\cdots N\}_2$ hydrogen bonding synthons 2) confirm the possibility of double proton transfer in the excited state, leading to the low-energy band in the emission spectrum of L.

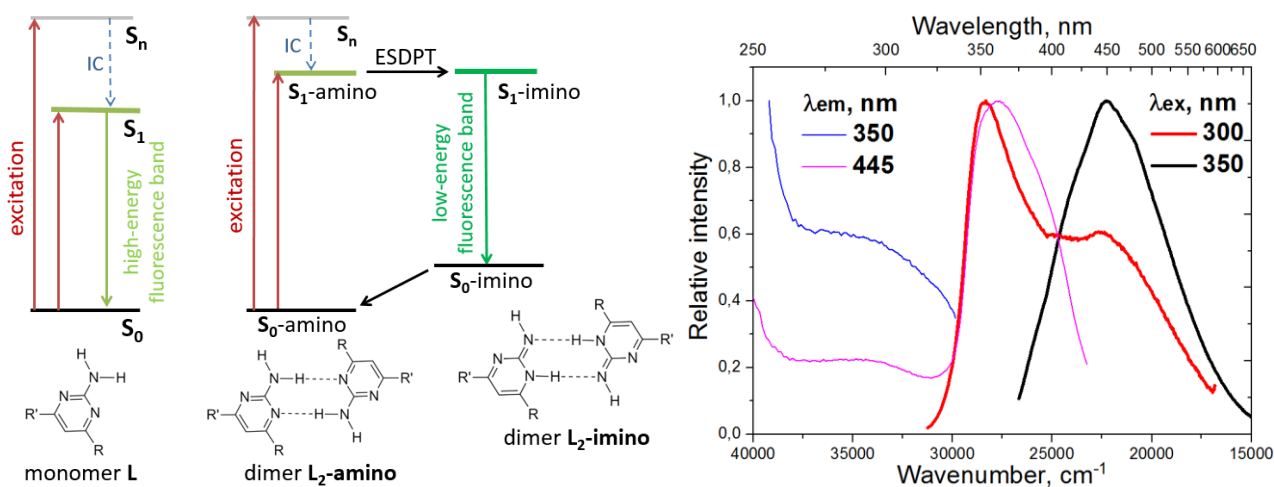


Fig. 1. A simplified energy level diagram showing typical photophysical properties of pyrimidine derivatives in the solid state (left); excitation and emission spectra of L (right)

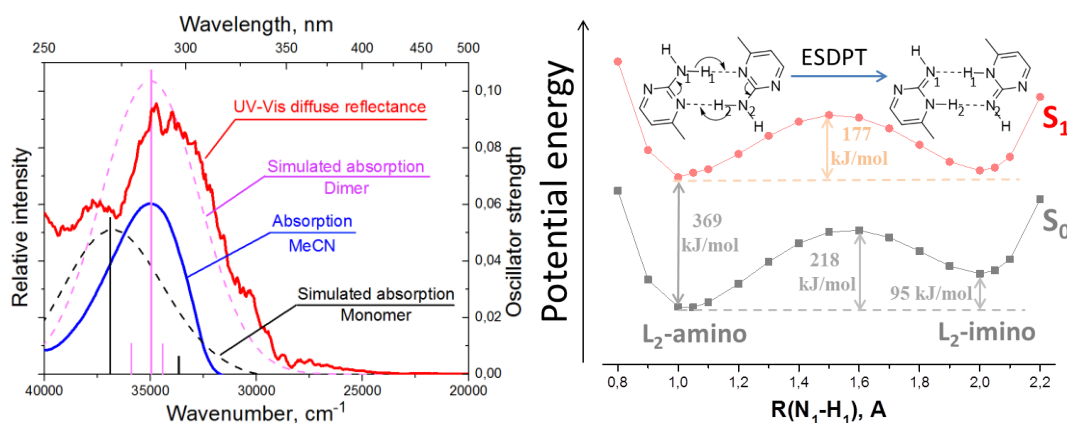


Fig 2. Experimental and simulated absorption spectra of L (left); 2D potential energy curves for the ground and first singlet excited states of L₂ with variation of N₁-H₁ and N₂-H₂ bond lengths (right)

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E. E. Stepanova, A. N. Maslivets

*Perm State University,
614990, Russia, Perm, Bukireva St., 15,
caterina.stepanova@psu.ru*

1,3-DIPOLAR CYCLOADDITION REACTION OF FUSED 1H-PYRROLE-2,3-DIONES WITH NITRONES: A DIVERGENT APPROACH TO PYRROLOISOXAZOLES*

Keywords: 1,3-dipolar cycloaddition, isoxazole, nitrones, 1H-pyrrole-2,3-dione, rearrangement.

Divergent synthesis is a promising trend in small molecules drug discovery [1, 2]. It allows to investigate the chemical space more efficiently and economically since diverse compounds collections are created from a limited set of reagents.