

Radiative and nonradiative recombination of pyrrolo[2,3-d]pyrimidine derivatives

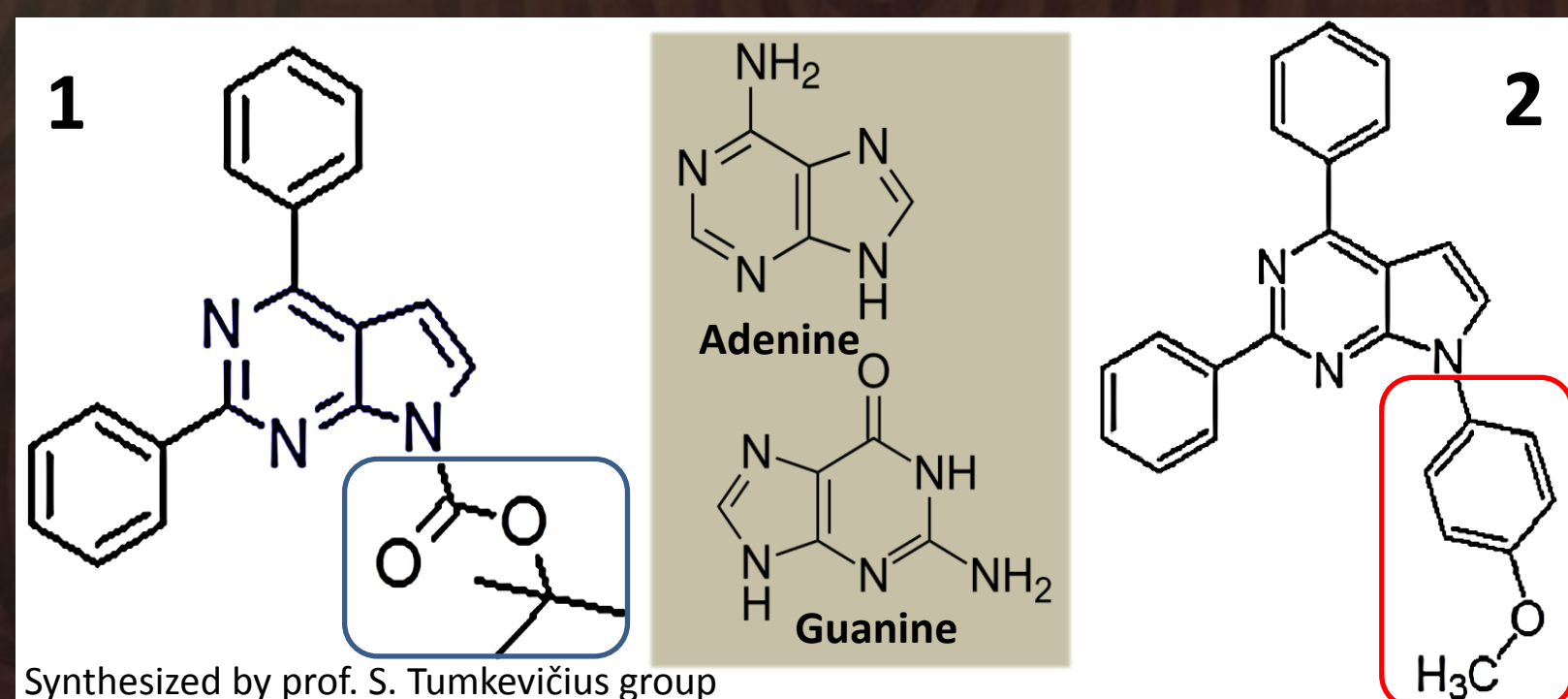


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The performance of the organic optoelectronic devices, such as OLEDs, solar cells and field transistors, strongly depends on molecular and photophysical properties of organic materials. Pyrrolo-pyrimidine derivatives demonstrate antiviral, antibacterial and antitumorous properties. They also share similar structure with two of the four DNA nucleobases – adenine and guanine. Efficient blue fluorescence of pyrrolo-pyrimidine derivatives could lead to their successful applications as bio-sensors and labels. Thus, it is of great interest to elucidate and, eventually, control the photophysical properties of such compounds. Here, we analyze the fluorescence and phosphorescence properties of two pyrrolo-pyrimidine derivatives with substituents of different polarity.

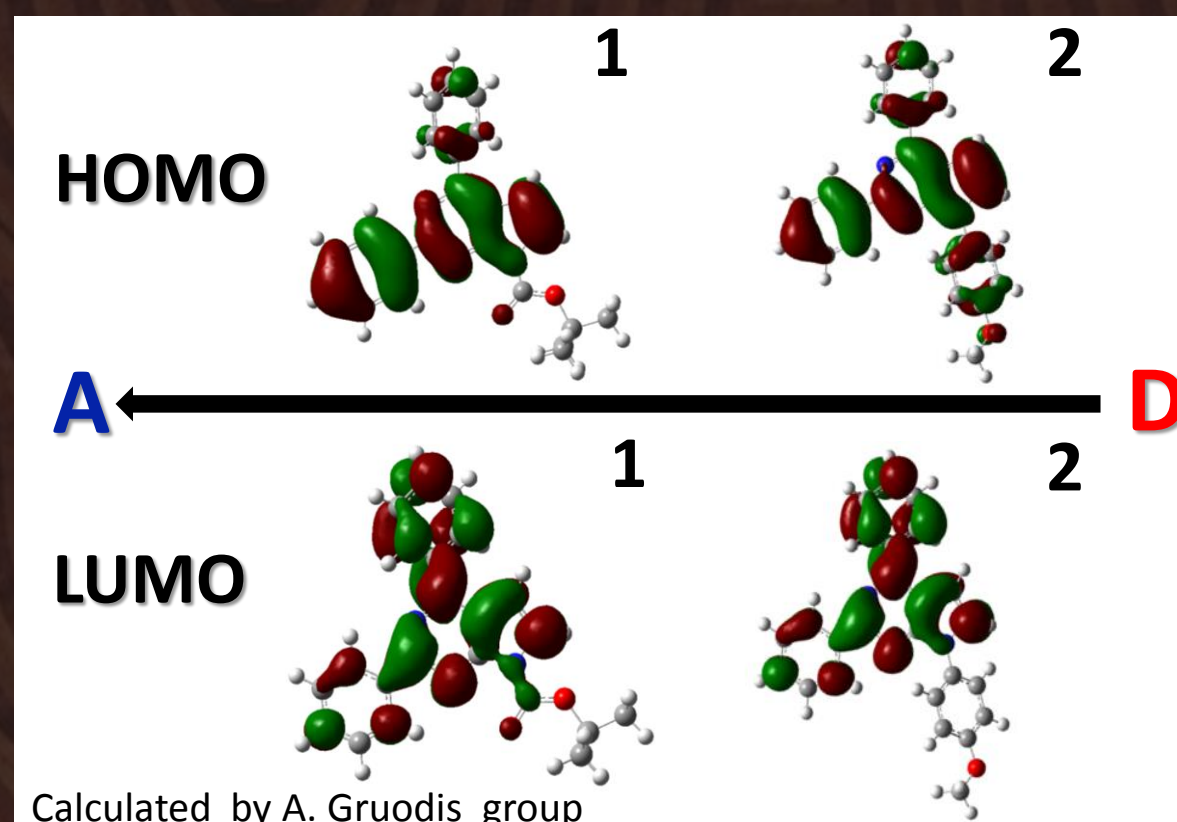
Investigation



Synthesized by prof. S. Tumkevičius group

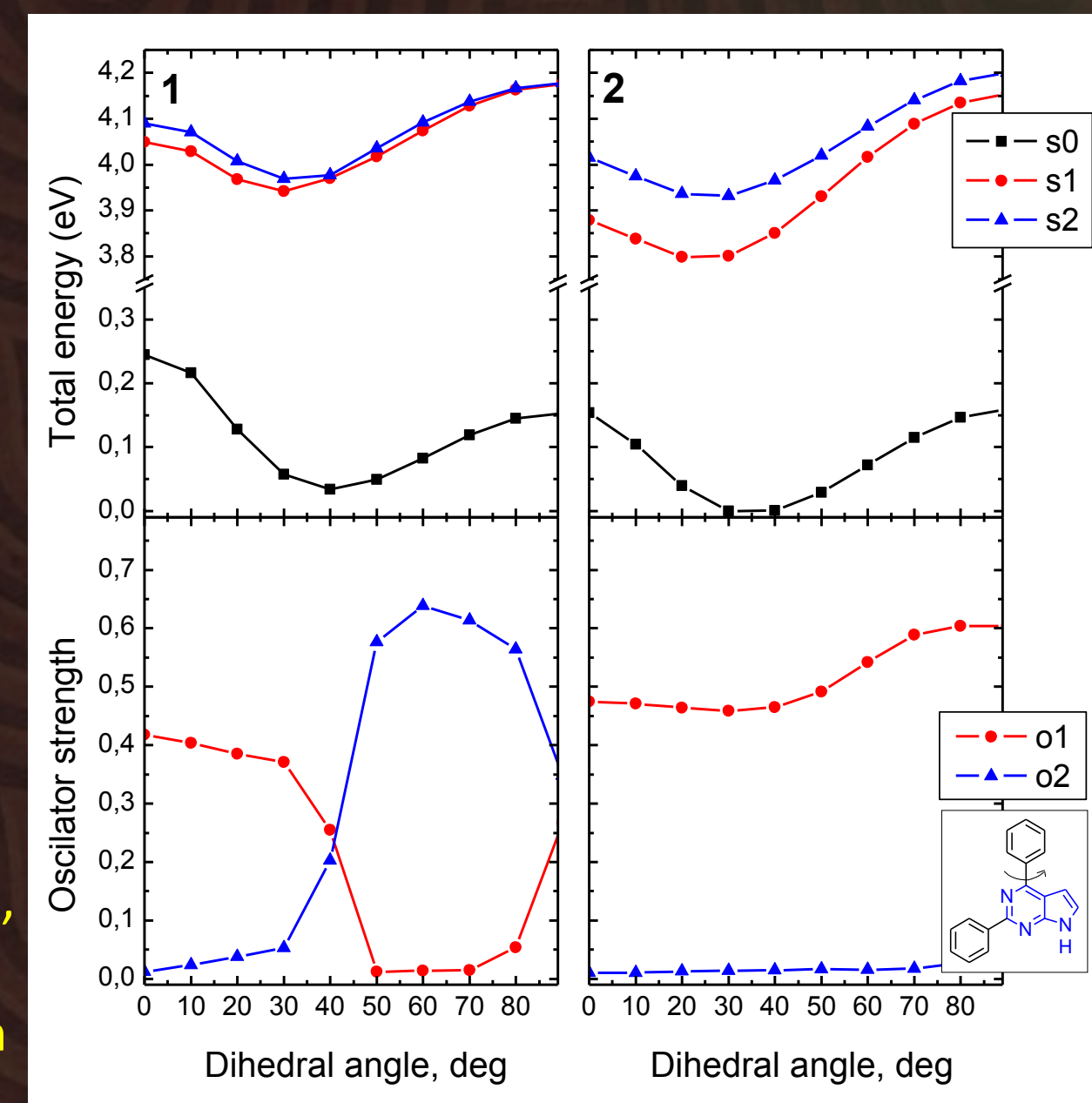
Pyrrolo-pyrimidine derivatives with tert-butoxycarbonyl (**1**) and phenyl-methoxy (**2**) substituents at the pyrrolo nitrogen atom were investigated in this work. The samples were prepared in Poly(methyl methacrylate) (PMMA) matrix. The fluorescence, phosphorescence and luminescence time characteristics were measured using Andor ICCD detector, allowing to control the delay and the signal enhancement of the measurement. The emission of the samples was registered in 15K temperature to decrease the nonradiative recombination efficiency. Experimental data were supplemented by quantum chemical calculations.

Theoretical calculations

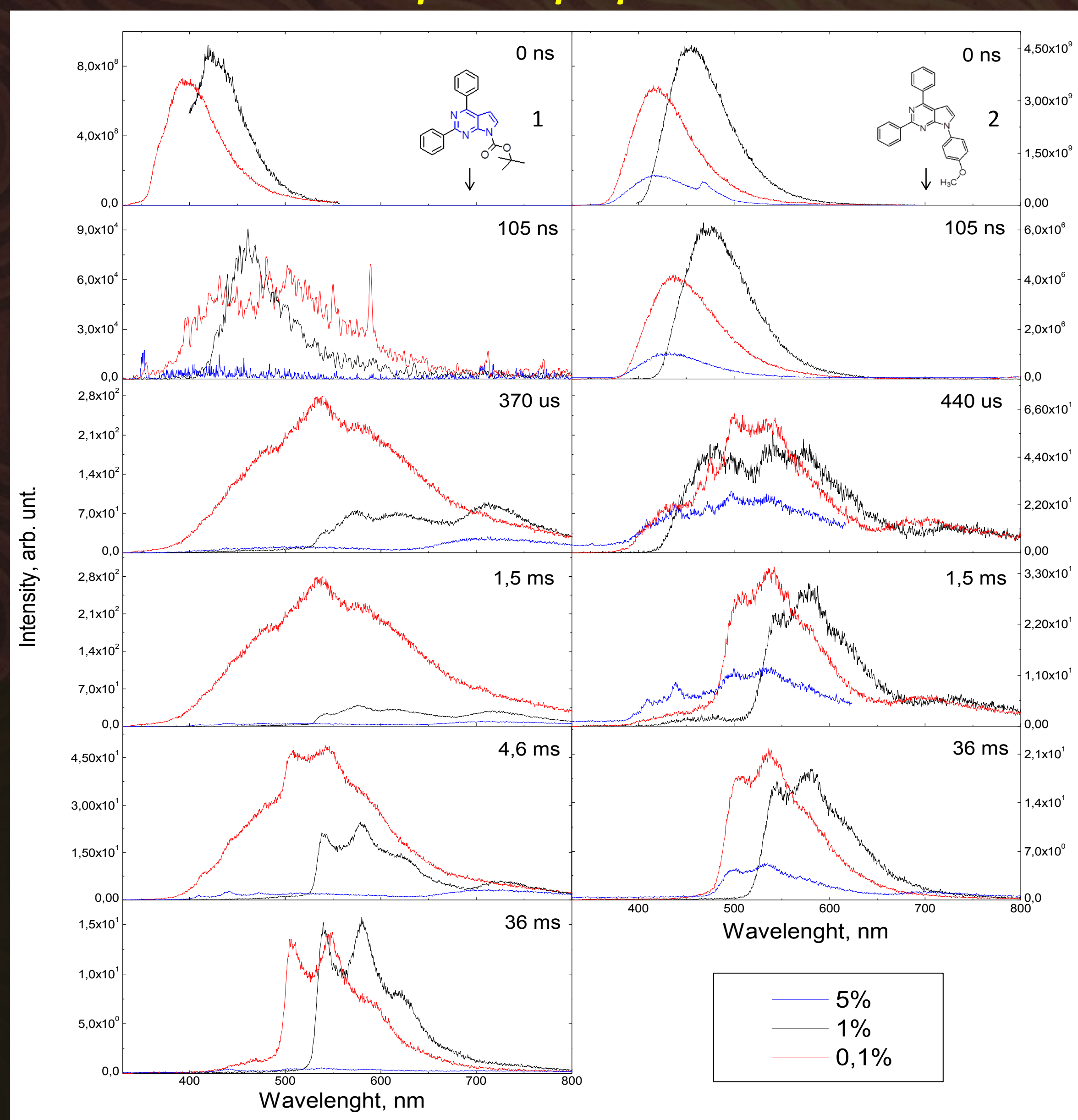


Calculated by A. Gruodis group

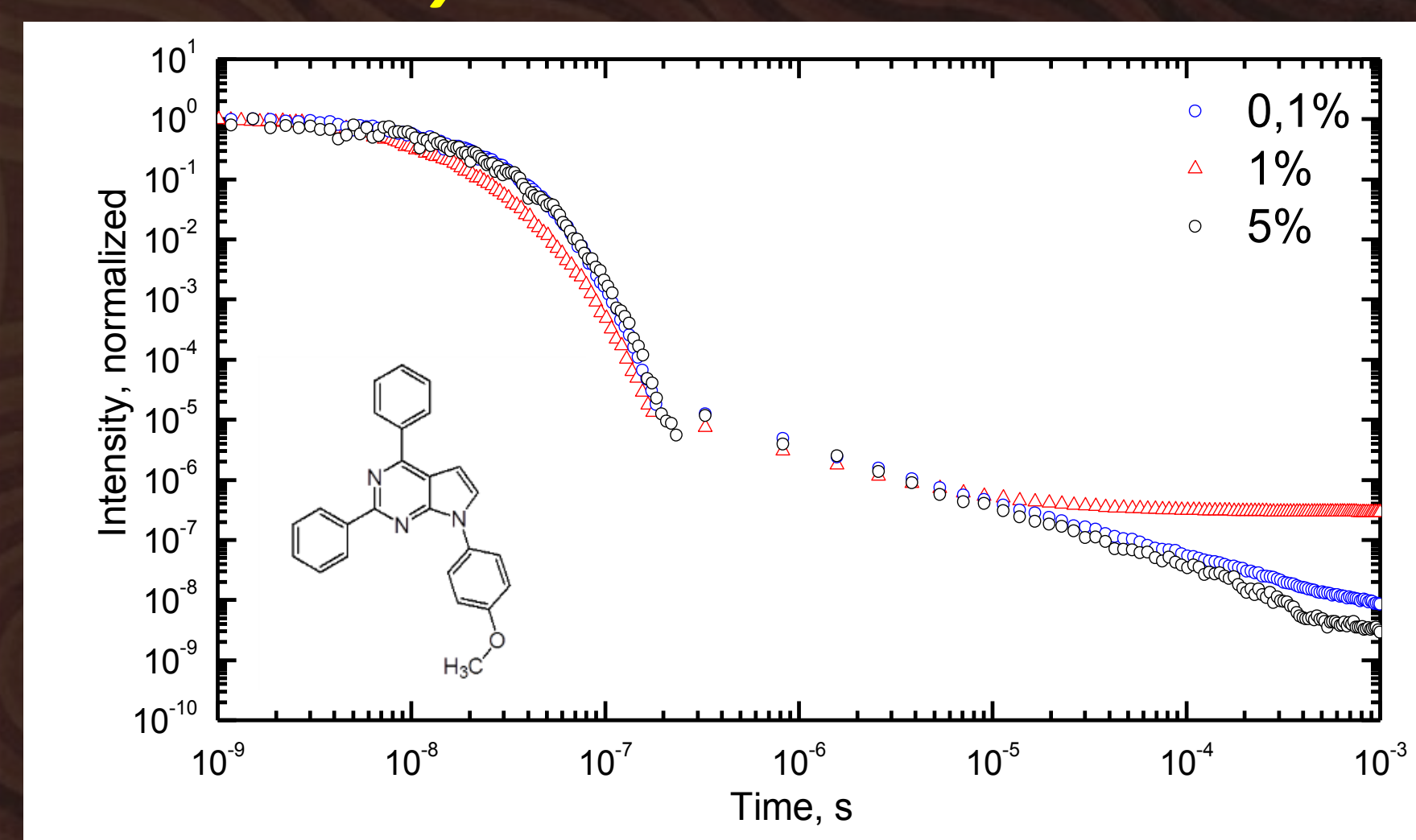
DFT calculations of molecular HOMO and LUMO orbitals (left) revealed intramolecular charge transfer character of the excited states, leading to twisting of the phenyl fragment at the 2-position of the pyrimidine ring. Addition of the acceptor-like tert-butoxycarbonyl fragment results in mixing of S1 and S2 energy states, while donor phenyl-methoxy functional group results in the separation of energy states, which is demonstrated by the dependency of the energy levels and oscillator strengths on the dihedral angle of the phenyl fragment (right).



Photoluminescence spectral properties



Transient dynamics



Both compounds exhibited one-exponential molecular fluorescence decay. The non-linear delayed fluorescence decay time implies to the triplet-triplet annihilation (TTA) process. The **1** compound demonstrated more expressed phosphorescence and less rapid TTA rate than the **2** compound.

The fluorescence is thought to be prevailed by the emission of the charge transfer state. The fluorescence spectrum of compound **1** peaks at 390 nm. The compound **2**, bearing a donor-like phenyl-methoxy group, demonstrate red-shifted spectrum at 415 nm. Both processes last for about 120 ns.

The delayed emission of compounds **1** and **2**, registered with a delay of 370 μ s and 440 μ s respectively, is located at 430 nm for compound **1** and 440 nm for compound **2**.

Both compounds share very similar phosphorescence spectra, with strongly expressed vibronic structure and are registered after a delay of 36 ms. The maxima of the phosphorescence spectra of compounds **1** and **2** are positioned at 500 nm and 540 nm for samples with 1% mass ratio of the compound to the host matrix.

Conclusions

The photoluminescence emission is influenced principally by the singlet energy states and polarity of the substituents. The compound with acceptor-like tert-butoxycarbonyl fragment demonstrates more rapid energy relaxation from the singlet states, increased intersystem crossing and more expressed phosphorescence in comparison to the compound bearing donor phenyl-methoxy functional group.