

Transistor is one of the most influential inventions of present times, which allowed for blossoming progress in modern electronic devices. In a typical bipolar transistor small current flowing between the gate and source electrodes controls much stronger current flowing between electrodes of the source and drain. Continuous progress in construction of complicated electronic devices, like increasingly powerful computers, requires the use of huge number of electronic elements, including transistors, in a small volume of a device and removal of heat created by the flowing currents. Miniaturization requires new look on the construction of a transistor. Particularly attractive choice, although difficult, is use of photons as the signal carriers and single dye molecules in a solid matrix for control of the emission of these photons.

The only one, up to now, construction of the optical single-molecule transistor was proposed by Vahida Sandoghhdara group, publication in *Nature* 460 (2009) 76-80. In technically advanced experiment, performed at 1.4 K, they observed weak absorption of tightly focused laser beam, when the light beam came into resonance with the zero-phonon line of the $S_0 \rightarrow S_1$ transition of a single molecule. Controlling the light intensity of a second laser, in resonance with the vibronic transition of the molecule, they were able to control, in some range, the intensity of transmitted light of the first laser. Experimentally difficult approach and fact, that they analyzed weak change of a strong signal may question practical use of the proposed construction of the optical transistor.

In the present project we propose a new, original solution of the optical transistor. The stream of photons, emitted by a single molecule excited, with the aid of first laser, to its singlet S_1 state will be controlled with the aid of second laser transferring this molecule to the triplet T_1 state. The proposed idea of the optical transistor is experimentally simpler, and the fluorescence signal should be stronger than the background level.

Single molecule of organic dye, excited to the S_1 state emits bunches of photons separated by dark periods, when this molecule undergo intersystem crossing to the long-lived triplet state T_1 . For single-molecule studies we chose molecules which can emit a big number of photons. It means, that in spite of high absorption cross section (for the $S_0 \rightarrow S_1$), high fluorescence quantum yield (for the $S_1 \rightarrow S_0$) and good photo-stability, the important requirements are low yield of transition to the triplet state T_1 and short lifetime of this state. It comes immediately, that by controlling population of the triplet state we may control the number of fluorescence photons emitted by the molecule. Such the simple idea is however difficult to be practically realized.

The simplest solution to control population of the T_1 state seemed to be by direct, $S_0 \rightarrow T_1$, intersystem crossing absorption. This transition is spin forbidden and can be only allowed by the weak spin orbit coupling. The only chance to overcome the forbidden transition is to perform experiment at very low temperature (1,5 K), when optical transition is concentrated in the narrow zero-phonon line, and to use a narrow-band and powerful cw laser emitting light in resonance with the transition. This approach requires precise knowledge about the energy gap S_0 - T_1 . Unfortunately, this information is not known for the systems appropriate for the single-molecule studies. Low lying triplet state T_1 is deactivated by the non-radiative channels. Principal investigator of this project tried, over several last years, to detect phosphorescence of the molecules like terylene, but without success. From the fluorescence intensity correlation function we only know the kinetic parameters, population and depopulation rate constants of the triplet state, but not the energy of this state.

In the present project we propose solution which does not require knowledge about the energy separation S_0 - T_1 . Population of the T_1 state will be controlled by the triplet energy transfer (in the Dexter exchange mechanism) from the excited triplet state of a matrix, $T_1H \rightarrow T_1$. Such the idea appeared to be possible only recently, when we observed single molecules of terylene in a 2,3-dichloronaphthalene single crystal (publication in preparation). It is a new system, not investigated before. Due to the presence of heavy atoms (chlorine) the crystal emits phosphorescence with the (0, 0) transition at around 487 nm. We thus know the wavelengths of the light required for the $S_0H \rightarrow T_1H$ excitation. Furthermore, the narrow-band, tunable and powerful cw lasers for this spectral range are commercially available. The important advantage may be the fact, that molecules of 2,3-dichloronaphthalene in the crystal structure are statistically oriented in one of two directions, "up" or "down". Such the statistical dipolar disorder leads to a distribution of the energies of the host and guest excited states, and the dispersive energy transfer is strongly limited at the low temperatures. We expect, that by appropriate choose of a single molecule and the wavelength of a "487 nm" laser we shall be able to optimize the energy transfer channel: $S_0H \rightarrow T_1H \rightarrow T_1$.

Investigation will be performed with four new systems. We plan to study single molecules of terylene and dibenzoterylene in two crystalline matrices, 2,3-dichloronaphthalene and 2,3-dibromonaphthalene. By careful investigations of the fluorescence intensity correlation function we shall obtain information about the population and depopulation rate constants of the triplet T_1 state. Comparison of the results should provide additional information about the external heavy-atom effect at the single-molecule level.

Realization of the project requires access to appropriate set-up and advanced knowledge of the investigators. The set-up, a "home-made" confocal microscope for single-molecule studies within the broad temperature range is available in the Institute of Physics. We have only to purchase a narrow-band cw laser for the spectral range around 487 nm, to excite the T_1H state.

Experiments performed in Warsaw will be supplemented by the single-molecule spectroscopic (SMS) study at 1.5 K in the Leiden University (in the laboratory headed by Prof. Michel Orrit). SMS technique, where a narrow-band spectrally tuned laser is used as the excitation source, allows to have several single molecules in the illuminated spot and provides better signal-to-noise ratio than the single-molecule detection (SMD) with a broad-band laser (in this case we may have only one single molecule in the illuminated spot), which is used in the Warsaw laboratory. Principal investigator of the project has deep experience with using both, SMS and SMD techniques. Recently, he was invited to prepare a review article for the prestigious journal *Chemical Society Review*, themed issue: "Single-molecule optical spectroscopy". Article: B. Kozankiewicz and M. Orrit, "Single-molecule photophysics, from cryogenic to ambient conditions", *Chem.Soc.Rev.* 43 (2014) 1029-1043, was published with the artistic figure of a Warsaw set-up on the cover page of the issue.