Upper Electron-Excited States in Coelenterate Bioluminescence

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Bioluminescence is a result of chemiluminescent oxidative enzymatic reactions. The theories of chemiluminescence and structure of the molecules predict that the process of bioluminescence may involve upper electron-excited states of the bioluminescent emitter molecule. It is believed that organic peroxides decompose to form nπ*-states of organic substances located at carbonyl groups. The bioluminescent emitter is supposed to be a heterocyclic compound with high fluorescence yield. It is specified by the upper singlet and triplet excited states of nπ*-type (Fig. 1) with excitation located on carbonyl groups. Generation of an excited carbonyl group of the similar compounds is to be followed by population of lower-energy singlet states, e.g. through intramolecular non-radiative transitions $T_{n\pi^*} \sim\sim\rightarrow S_{\pi\pi^*}$. This process is permitted as transition between the levels of different both orbital nature and multiplicity (El Sayed rule). Emission of light is the final stage of the bioluminescent process (Fig. 1).

The hypothesis of activity of upper electron-excited states of the bioluminescent emitter was first proposed by N.S. Kudryasheva and D.N. Shigorin. It was experimentally confirmed for bioluminescent emitter of bacteria. Application of the hypothesis to bioluminescent emitters of other organisms (fireflies, coelenterates, etc.) is of great interest now.

This investigation was aimed to examine activity of upper electron-excited states in coelenterate bioluminescence. Bioluminescent spectra of mutant of obelin F88H in the presence of pyrene were studied. Pyrene is a dye molecule serving as foreign energy acceptors in the bioluminescence system (Fig. 1).The weak sensitized fluorescence of pyrene was found. Since the energy of the fluorescent states of pyrene (28500 cm^{-1}) exceeds that of the bioluminescent emitter (23800 cm^{-1}) and its absorption spectrum does not overlap with the bioluminescence spectrum, the trivial light absorption and intermolecular resonance S-S transfer were excluded. This result confirmed activity of upper electron-excited states in coelenterate bioluminescence.

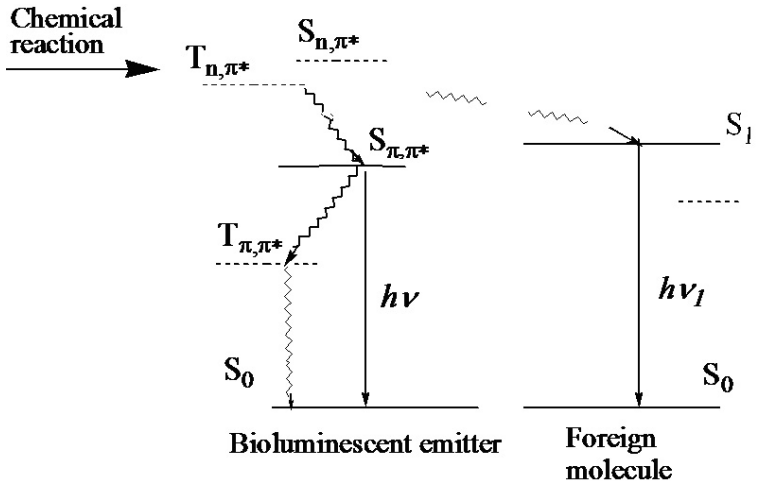

Fig. 1: Yablonski diagram of bioluminescent emitter and exogenous fluorescent compound.