# Concurrent ultrafast twisting and proton transfer reactions in new pyrano[2,3-*c*]pyrazole derivatives

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Fused pyrazole derivatives represent an important class of organic compounds and find different applications as functional materials.[1] As it was observed before, these dyes exhibit characteristic dual emission because of excited-state intramolecular photon transfer (ESIPT)[2]. Excitation of the ground sate pyrazole molecule immediately produces emission of normal form which may undergo ESIPT generating tautomer with the emission in the red spectral region.[2] In this work we present a detail investigation of ultrafast excited and ground state proton transfer pyrano[2,3-*c*]pyrazole compounds, containing electron-donating groups.

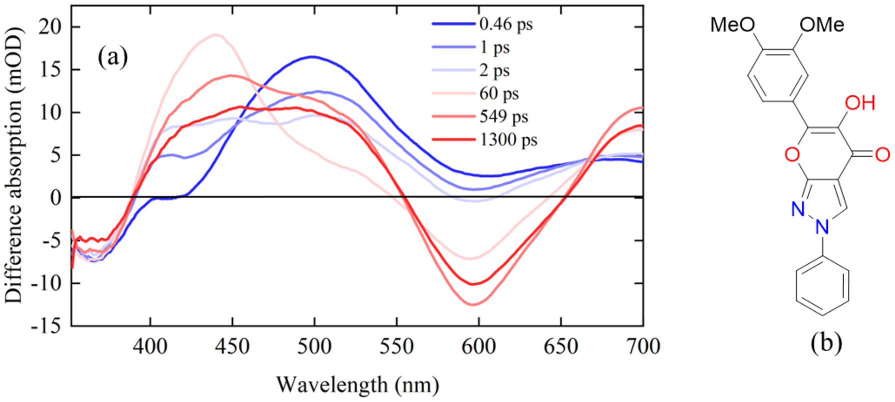

Fig. (a) TA spectra, of pyrano[2,3-*c*]pyrazole compound and (b) the structure of investigate molecule.

Fig.1. shows the transient absorption (TA) spectra of pyrazole compound, containing two methoxy substituents, dissolved in methanol (MeOH) and represents the structure of the molecule. The earliest spectra demonstrate distinct dual emission at 480 nm and 600 nm due to excitation of normal (N*) and tautomer (T*) emission. As we can observe, the T* state emission appears immediately after excitation, together with N* state emission. This suggests that ESIPT reaction occurs not only from the N* state, but a small fraction of proton transfer takes place directly from the excited Franck-Condon state. Furthermore, at 60 ps probe time, the TA demonstrate a decrease of excited state absorption at *ca.* 520 nm. The TA simultaneously with kinetic fluorescence measurements revealed that this change is related to the formation of twisted intramolecular charge transfer (TICT) state which in MeOH is stabilized in 5 ps. Due to formation of TICT state in MeOH, ESIPT reaction is reduced and takes place in a time scale of 300 ps. Further, we investigated ground state proton transfer (GSIPT) using pump-dump-probe (PDP) spectroscopy. The dump pulse was set in resonance with the T* emission, to prepare a short-lived tautomer in the ground state. By simultaneously measuring the PDP spectra and kinetic traces, we observed a very fast GSIPT reaction with time constant of 8 ps. These results are of great value to fully describe the photocycle in these new compounds, providing a deeper understanding of dynamical electron-donation group effects on tautomerization.

## References

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