# Effect of hydrogen bond on the charge transfer dynamics in the excited state of coumarin 343: experimental and theoretical study

**Xiaochun Liu, Hang Yin, Hui Li, Dajun Ding, Ying Shi*** [1]

* Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China

**Synopsis** Excited state intramolecular charge transfer (ICT) plays a crucial role in photosynthesis and chemical energy conversion. It is important to understand the influences of intra- and inter-molecular hydrogen bond on ICT for purposeful adjustment of this process. This work reports the excited state ICT of coumarin 343 (C343) in acetonitrile (ACN) and dimethylsulfoxide (DMSO) solvents by experimental transient absorption spectrum and theoretical DFT/TDDFT methods. Ultrafast dynamic analysis shows that the ICT is noticeably accelerated in DMSO. Theory calculation suggests that this difference arises from different excited state hydrogen bond strengthening and weakening mechanisms.

C343 with an ICT type excited single state displays great sensitivity to the hydrogen bond acceptance ability of solvent and this sensitivity increases in the excited state [1]. Inevitably, this unusual behavior is related to intermolecular hydrogen bond interaction. In order to get a better understand about the different impact mechanism of intramolecular and intermolecular hydrogen bond interactions on the excited state ICT of C343, we conduct experimental and theoretical analysis.

The femtosecond transient absorption spectrums of C343 in ACN and DMSO are performed with the excitation at 400nm. The Global fitting results of ultrafast kinetic lifetimes are shown in Table 1. We attribute the component with a lifetime of several picoseconds as the decay time of ICT for C343. The lifetime of ICT process is noticeably reduced from about 10ps in ACN to 5ps in DMSO.

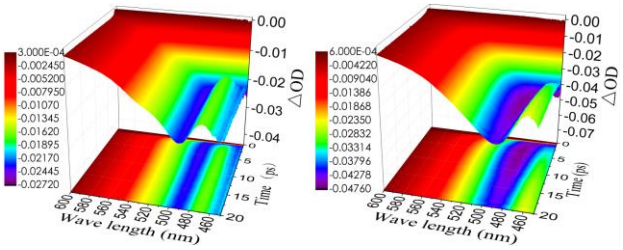


**Figure 1.** 3D image plots of the transient absorption for C343 in ACN (left) and DMSO (right) after excitation at 400 nm.

**Table 1.** Transient absorption kinetic lifetimes of C343 in ACN and DMSO by global analysis.

| solvent | $\tau_1$(ps) | $\tau_2$(ps) |
|---|---|---|
| ACN | 0.1155 ±0.0139 | 10.49 ±2.231 |
| DMSO | 0.1746 ±0.0265 | 5.021 ±0.001 |

DFT/TDDFT calculations show that DMSO can 'open up' the intramolecular hydrogen bond to form intermolecular hydrogen bond with C343. The properties of intramolecular and intermolecular hydrogen bond in excited state for C343 monomer, C343-DMSO complex and their effects on the process of excited state ICT have been investigated by detailed comparative analysis. It has been confirmed that ICT occurs between HOMO and LUMO for both C343 monomer and C343-DMSO complex in the first excited state. In addition, our calculations results show that the intramolecular hydrogen bond interaction is strengthened while intermolecular hydrogen bond interaction is weakened upon exciting to ICT state. DMSO solvent can not only break the intramolecular hydrogen bond but also alter the mechanism of excited state hydrogen bond strengthening.

## References

[1] O.F. Mohammed *et al.*2009 *Angewandte Chemie* **48** 6251

[1] E-mail: shi_ying@jlu.edu.cn