Transient Absorption Measurement of Highly Luminescent Materials

(*Unisoku Co., Ltd.*) ○Tatsuo Nakagawa

Keywords: transient absorption spectroscopy; fluorescent lifetime; RIPT method; TCSPC method

In the study of luminescent materials, measuring luminescence spectrum and/or luminescence lifetime would be the first step, but they don't necessarily tell us why the yield of luminescence improves or decreases, while other approaches may provide us important information. In this talk, I mainly focus on time-resolved measurements, luminescence lifetime and transient absorption (TA).

From the viewpoint of instrumentation, technical complexity increases in time-resolved measurement compared to steady state absorption / fluorescence measurements. First, regarding acquisition of luminescence lifetime, measurement techniques are largely different between fluorescence and phosphorescence due to time region they lie. Specifically, fluorescence lifetime which is the relaxation process of excited singlet state typically lies in the range of 0.1 ns to 100 ns, and advanced technique, Time-Correlated-Single-Photon-Counting (TCSPC), is often used. Easy-to-use instruments are now commercially available, so it is relatively easy to acquire fluorescence lifetime. On the other hand, phosphorescence which is relaxation process of excited triplet state occurs in the time range of microseconds to milliseconds, so direct measurement of emission intensity decay is possible and degree of technical difficulty is decreased.

Techniques for TA also differ dependent on time region of reaction processes of interest. In TA, probe light is required in addition to the excitation light. When continuous-wave light is used for the probe light, its intensity and response time of detector determines the time resolution, and it is typically several nanoseconds. On the other hand, Pump-Probe method, which utilizes a probe-light pulse and a pump-light pulse which are emitted and split from an ultrafast laser makes it possible to enhance time resolution to femtoseconds, while time region longer than nanoseconds is difficult to be measured. Therefore, by conventional TA techniques, systematic measurement and study of excited singlet state which lies in the time range of nanoseconds has been limited so far.

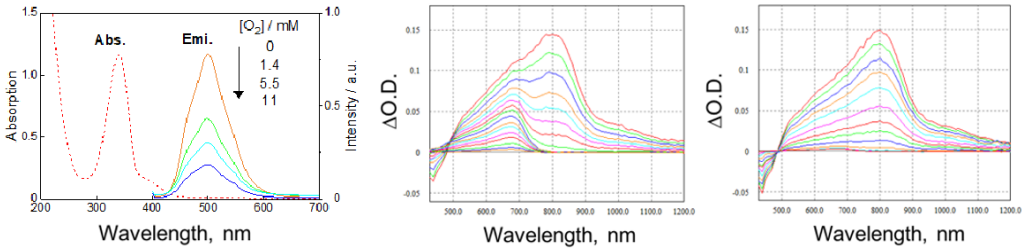

Figure 1. Absorption and emission spectra of CPP in THF, and TA spectra with and without oxygen

For these several years, we have been developing a new TA technique, Randomly-Interleaved-Pulse-Train (RIPT) method [1] in which pulse trains are utilized for probe light. The RIPT method has enabled to measure TA from subnanosecond to millisecond, and another remarkable feature of this method is its capability to discriminate luminescence signal from TA signal. For such a new technique, it is very important to evaluate its validity and reliability. Since manufactures like us are often not familiar with materials and its chemistry, so we are actively collaborating with many research groups and are trying to apply the RIPT method to various types of photofunctional materials, some of which are highly luminescent, and over 30 papers have already been published.

Figure 1 is one of examples and shows fluorescence spectra and TA spectra of Cycloparaphenylenes (CPP) in THF by collaboration with Osaka University and Nihon University [2]. The quantum yield of its fluorescence is > 0.8 in some conditions, but it decreases with increasing the concentration of oxygen. It is well acknowledged that the excited triplet state is quenched by oxygen because the ground state of molecule oxygen is triplet, but the reason of quenching of excited singlet of CPP was unclear only from fluorescence measurement. However, lifetime of 1~10 ns and strong fluorescence makes it difficult to measure TA by conventional methods. The RIPT method can change this situation, and we could obtain conclusion that oxygen enhances intersystem crossing from the fact that TA spectra of triplet is clearly increased by increasing oxygen concentration. This study shows that TA measurement by the RIPT method is very useful in highly luminescent materials and elucidation of luminescence-related various mechanism.

In the RIPT method, high time resolution is achieved by calculating time difference between a pump-light signal and each probe-light signal in a pulse train recorded in an oscilloscope. This technique is analogous with TCSPC in which time difference between excited light pulse and a single photon of fluorescence is measured. We recently succeeded in incorporating TCSPC capability to the RIPT system only adding a single photon counting detector. As a result, we can now obtain both TA curves and luminescence decay curves with a single instrument. We would like to enhance its performance and reliability by collaborating with many researchers.

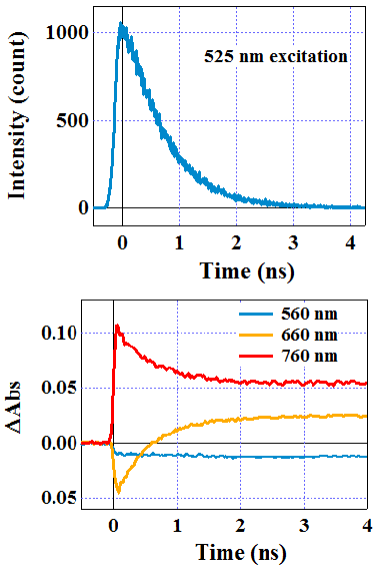

Figure 2. Oscilloscope-based TCSPC fluorescence decay and RIPT-TA temporal profile of MK2 dye in toluene

1) T. Nakagawa, K. Okamoto, H. Hanada, R. Katoh, *Opt. Lett.*, **2016**, *41*, 1498.
2) T. Suenobu et al., *J. Phys. Chem. A* **2020**, *124*, 1, 46