

## Simultaneous Measurements of Transient Absorption and Luminescence by Using a Randomly-Interleaved-Pulse-Train (RIPT) Method

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Nanosecond flash photolysis, one of transient absorption (TA) measurement methods, is widely used in various fields of photochemistry to directly observe elementary photophysical processes as well as photoreactions in the photoexcited state followed by subsequent slower processes in the time range usually from  $\mu\text{s}$  to  $\text{ms}$ . On the other hand, since the emission of luminescent compounds usually lasts from sub-ns to  $\mu\text{s}$ , the strong luminescence frequently conceals the initial-stage TA signal of great interest. Alternatively, TA measurement by femtosecond pump-probe technique is essentially unsusceptible to the luminescence, but can cover only up to a few nanoseconds although reactions of interest often take time much longer than nanoseconds.

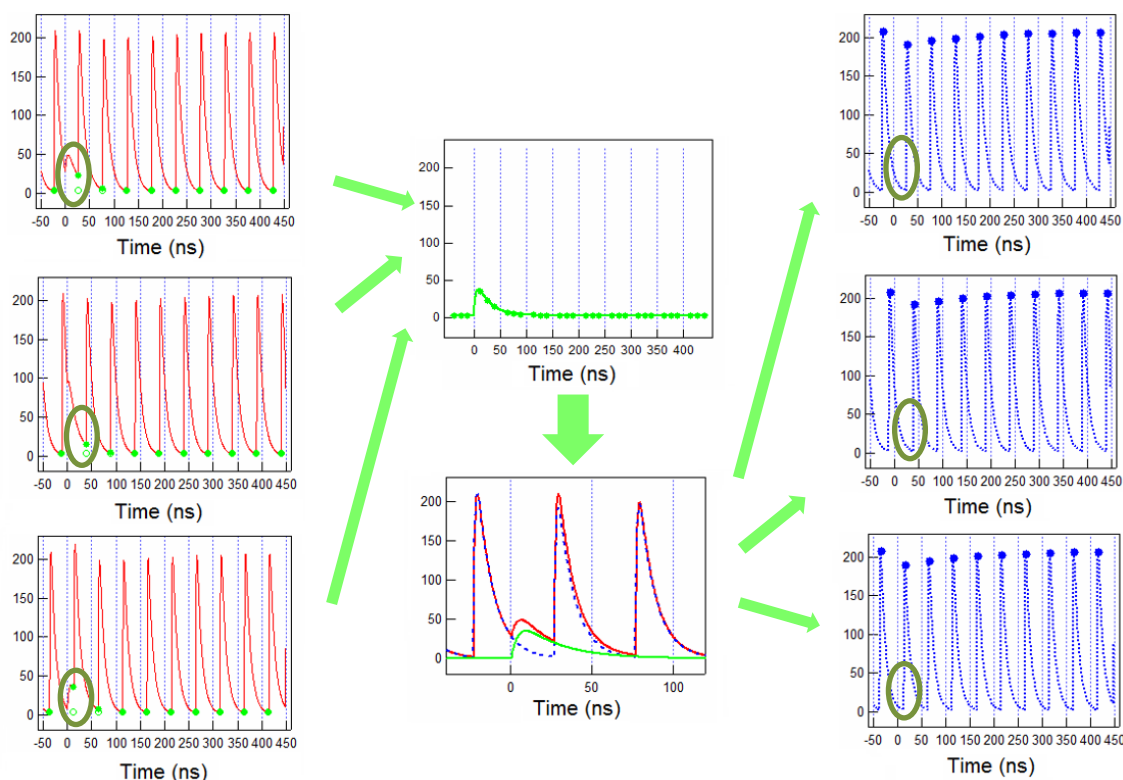


Figure 1. Emission signal extraction in the RIPT method.

Recently, we have proposed a novel technique, RIPT (Randomly-Interleaved-Pulse-Train) method, and constructed a prototype of TA spectrometer based on the RIPT method.<sup>[1]</sup> Usage of the pulse train for probing, the timing of which is asynchronous with respect to the single pump pulse, affords sub-ns time resolution and wide dynamic range up to milliseconds by the repeated pumping cycle since the delay time automatically varies due to the asynchronicity. Further unique feature of the RIPT method is the capability of discriminating the luminescence signals from the probe signals, thus, not only TA curves but also luminescence temporal profile can be obtained (Fig. 1). Of particular note is that the sub-ns time resolution is not always necessary for the detection of luminescence for the purpose of exact discrimination of the luminescence from contaminated TA signals. Furthermore, the capability of simultaneous measurements of TA and luminescence with use of the same single instrument is obviously like nothing else.

We applied the RIPT method to highly luminescent compounds such as tris(2-phenylpyridinato)iridium(III) complex ( $\text{Ir}(\text{ppy})_3$ ), one of the most successful organic light emitters for OLED, and a core-shell type quantum dot ( $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ ). Correct TA measurements for these compounds have technically been difficult so far by typical nanosecond flash photolysis technique due to the pollution by luminescence signal, however, we have successfully obtained correct TA and emission spectra simultaneously upon laser excitation at  $\lambda = 355$  nm, and confirmed that their decay time profile coincides with each other.

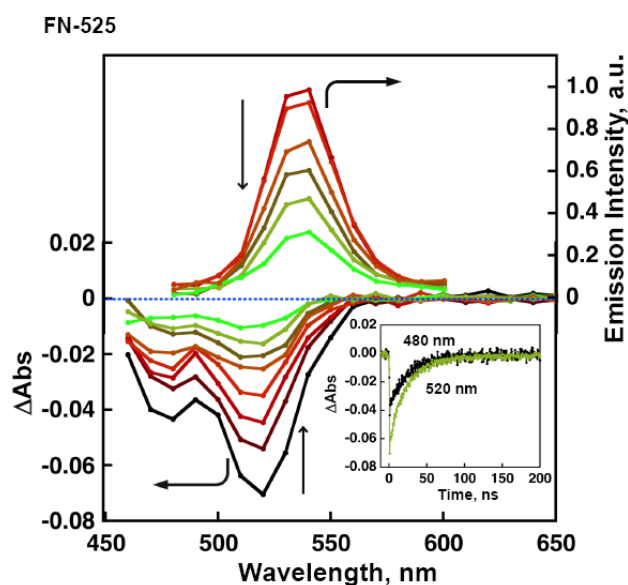


Figure 2. Simultaneously obtained transient absorption spectra (lower traces) and emission spectra (upper traces) of core-shell type quantum dot ( $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ ; FN-525-A) dispersed in deaerated THF-toluene mixed solvent (7:3 v/v). Both spectra were observed at  $t = 0, 4, 8, 12, 20, 24, 32,$  and  $44$  ns by the RIPT method. Inset: Time course of  $\Delta\text{Abs}$  at  $\lambda = 480$  and  $520$  nm.

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#### References:

- [1] T. Nakagawa, K. Okamoto, H. Hanada, R. Katoh, *Opt. Lett.*, **2016**, 41, 1498. Highlighted by G. Donati, *Nat. Photon.*, **2016**, 10, 285; J. Yeston, *Science*, **2016**, 352, 669.