



Application Note 1070-215

Millisecond Time-Resolved Photoluminescence Measurements Using PPMS

Purpose

Time-resolved luminescence measurements under a high magnetic field (up to 9 T) and with temperature control over a wide range are not feasible with most available commercial systems. Furthermore, the supporting material to be used must be non-magnetic and the required optical fibers must withstand low temperatures (down to 1.9 K in this case). The Physical Property Measurement System (PPMS) from Quantum Design, available on GeMaC, Versailles (France) is equipped with a customized electro-optical probe composed of three optical bundles consolidated in one non-magnetic tube. This specific system allows performing millisecond time-resolved optical measurements in a broad temperature range (from 1.9 K up to 400 K) and with magnetic fields up to 9 T, by connecting both the light source and the detector to two different optical fibers, one used to deliver the excitation light to the sample and the other to collect the emitted light from the sample. The distance between the fibers and sample is adjustable, according to Figure 1. Samples are usually held in place in the support by using special glues. In order to perform low temperature luminescence measurements correctly, caution must be taken because these glues can also luminesce and contribute to the measured signal.

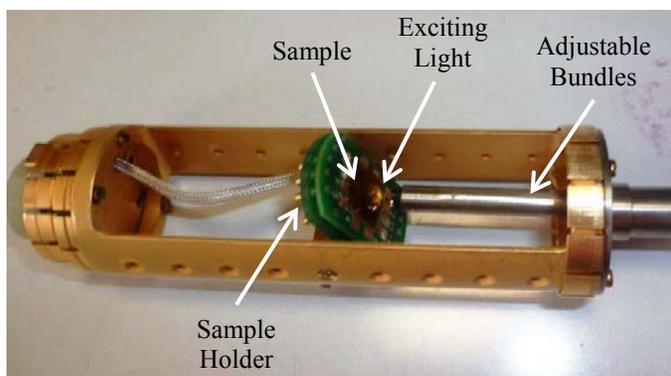


Figure 1. Scheme of the sample holder.

The light source used to excite the sample was a 6 W pulsed Xe light source (www.sarspec.com) in which the frequency of each pulse (with an average energy and a width of 48.6 mJ and 10 μ s, respectively) was controlled by a FeelTech FY21002S DDS Signal Generator. An RG645 long-pass filter was used in the excitation set-up. The emission light was recorded using a Single Photon Counting unit (H11890-01) from Hamamatsu (www.hamamatsu.com) coupled with a collimating lens and a long-pass filter (RG780), which helped to collect the highest number possible of photons and to remove any stray light or luminescence coming from the excitation source or other possible contaminants. No temperature variation was observed when irradiating the sample.

The scheme of the whole system used to perform the measurements is shown in Figure 2.

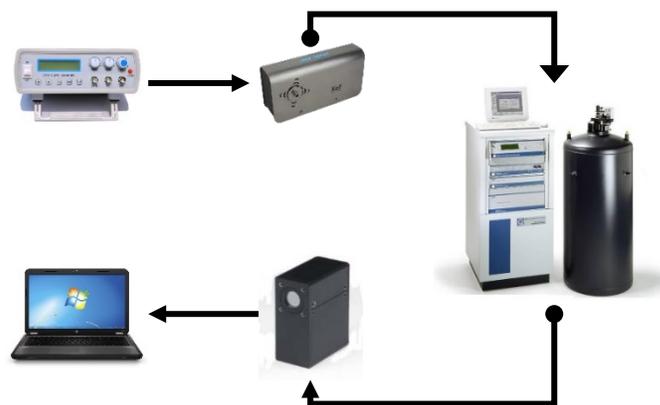


Figure 2. Diagram of the whole system used in this experiment.

When lifetime measurements were performed, the recorded decay showed two exponential components. The first one, with the highest intensity, had a lifetime in the tens of milliseconds range, corresponding to the fullerene molecules, whereas the second one, weaker, had a longer lifetime of 0.80 s. A control experiment revealed that the long component was the result of emission from the glue used (GE 7031). The respective phosphorescence emission spectrum is shown in Figure 3.

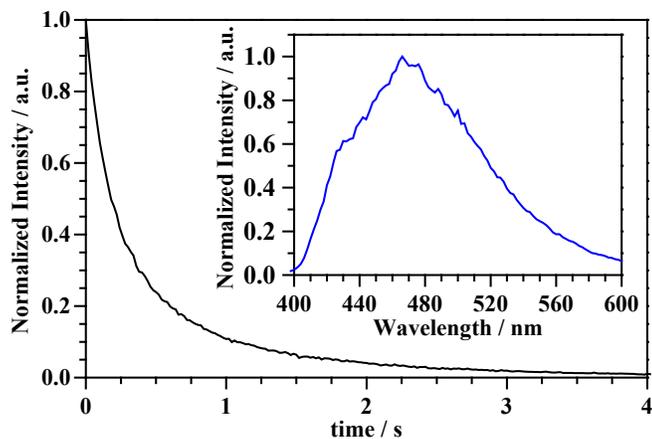


Figure 3. Phosphorescence decay ($\lambda_{\text{emission}} = 470 \text{ nm}$) of the glue used to fix the sample to the sample holder. The average lifetime yield is 0.80 s. The inset shows the phosphorescence emission spectrum. Both measurements were performed at 77 K.

The molecules studied were fullerenes C70 with 1% and 90% carbon-13 (C-13), both from MER Corporation. The fullerenes were dispersed in a Zeonex (a cyclo olefin polymer donated by Zeon Corporation), matrix. It is known that C-13 enrichment has an effect on the photophysical properties of these molecules, originating an

increase of the delayed fluorescence efficiency¹ and of the phosphorescence lifetime (at 77 K)² [2]. Also, excited fullerenes (in the triplet state) are paramagnetic, hence a strong magnetic field could influence the emission. An example of the results obtained is shown in Fig.4.

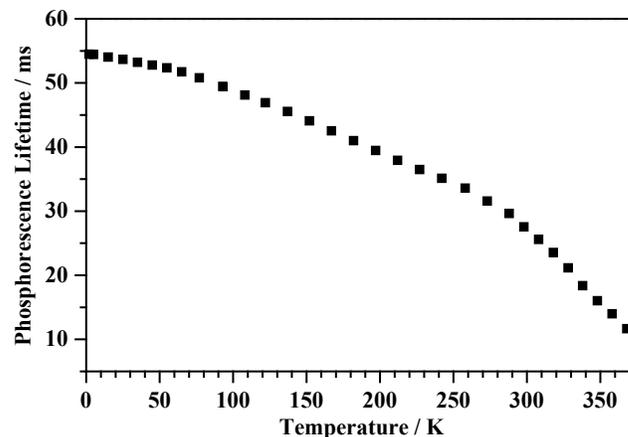


Figure 4. Phosphorescence lifetime of C70 1% C-13 in Zeonex versus temperature.

¹ Baleizão C., Berberan-Santos M. N. The brightest fullerene: a new isotope effect in molecular fluorescence and phosphorescence. *ChemPhysChem* 12, 1247–1250 (2011).

² Palmeira T., Fedorov A., Berberan-Santos M. N. Temperature dependence of the phosphorescence and of the thermally activated delayed fluorescence of 12C70 and 13C70 in amorphous polymer matrices. Is a second triplet involved?, *Methods and Applications in Fluorescence*, 2, 035002 (2014).

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