Supplementary Material

November 13, 2023

1 Multimodal Quantum Yield System

The experimental setup used in this study is a multimodal QY system that takes into account several crucial parameters for accurate evaluation of the iQY of UCNPs. These parameters include beam profile, scattering, and simultaneous measurements of the UCL along absorption at various excitation powers. The system was modified to extend the wavelength range of the UCL measurements from the NIR to the visible range and to allow for simultaneous UCL measurements of two wavelengths at two separate avalanche photodiodes (APDs). Fig. 1 presents a simplified sketch of the QY setup, which is described as follows:

The collimation module provides a collimated beam with vertical polarisation that is used to excite the UCNPs sample. The module consists of a 500 mW CW 976 nm laser diode (Thorlabs – BL976-PAG500), controlled by a digital driver (Thorlabs – CLD1015). The laser beam is collimated by lens L1 and guided by mirrors M1 and M6 to lens L6, placed at its focal length distance from the centre of the cuvette holder labelled as CH1, where a quartz cuvette with four clear windows containing the UCNPs in liquid solution is placed. Lenses L1 and L6 shape the beam with a Gaussian profile and narrow beam-width focused at the centre of the cuvette holders (CH1 and CH2). Flipping up mirrors FM3 and FM4 adds the option of performing measurements with a wider beam-width, shaped by the addition of lenses L4 and L5 on the beam path. The narrow beam-width is utilised to achieve high excitation power densities, whereas the wider one is used for low excitation power density measurements with high signal-to-noise-ratio.

Along the illumination path, right after lens L6, a beam profile arm is attached at a 90^o angle. The beam-splitter BS1 reflects around 2% of the light towards a CMOS camera (Thorlabs - DCC3240-X), which is precisely mounted at a point where the BS1 is equidistant from it and from the cuvette holders along the excitation path. This guarantees that the pictures collected by the camera are images of the profile of the beam that reaches the centre of the cuvettes. The beam-splitter BS2 is mounted equidistant from the cuvette holders CH1 and CH2. CH2 is for a blank cuvette containing solvent, the same as the UCNPs are diluted on, as a reference for the absorption measurements. Right after the cuvette holders, powermeters PM1 and PM2 (Thorlabs - PM100D) are

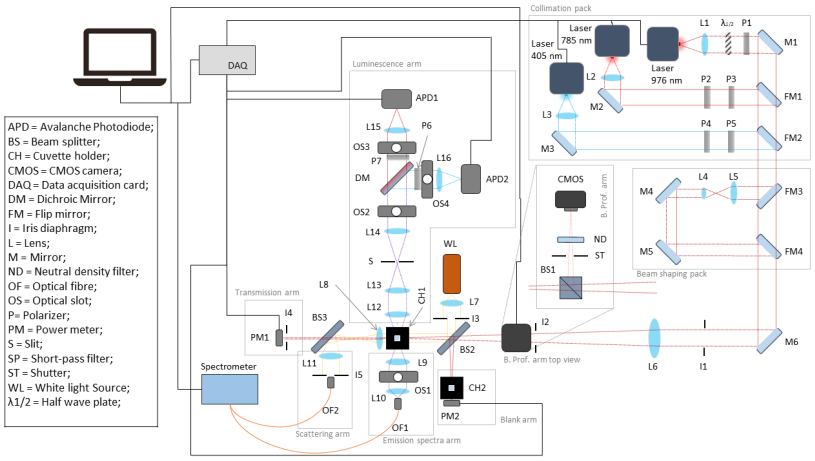

Figure 1: QY system for multiple wavelength emission.

mounted to measure the transmitted light that crosses through CH1 and CH2, respectively.

For the emission spectra measurement, the emission spectra arm is attached to CH1 at a 90^o angle in respect to the excitation axis. L9 collects the emitted light from the UCNPs at the centre of the cuvette and guides it through a short pass spectral filter (Semrock - FF01-890/SP-25) placed inside the removal optical slot OS1. The filtered light is focused to the tip of an optical fibre that is connected to a commercial spectrometer (Ocean Optics - QEPro-FL). The luminescence arm is mounted on the opposite direction in respect to the emission spectra arm. L12 collects the emitted light, collimates it, and L13 focuses the collimated light to the 1 mm aperture of a slit placed at the focal point of L13 and equidistant from L13 and L14. The slit ensures that only the light coming from the region with 1 mm in length at the centre of cuvette will reach the sensors of the APDs. The emission light, collimated by the lens L14, is split by a dichroic mirror DM (Thorlabs - DMLP550R). Wavelengths below 550 nm are reflected towards the APD2 (Thorlabs, APD440A2), which is optimised for visible range detection, while wavelengths above 550 nm are transmitted towards the APD1 (Thorlabs, APD410A/M), optimised for NIR detection. The optical slots, OS2, OS3, and OS4, accommodate spectral filters used to filter any stray light from the laser beam and to select a specific wavelength of the emission spectra to be measured. The polarisers P6 and P7 were oriented at the 53.4^o magic angle with respect to polariser P1 to eliminate any possible anisotropic effects resulting from the orientation of the UCNPs dispersed in the liquid solution. The lenses L15 and L16 focus the collimated and filtered light onto the sensors of the APD1 and APD2, respectively. The laser driver was controlled, and the data were collected using a Python software running on a laptop connected to a DAQ card (National Instruments - NI-USB6218) via a

USB cable.

The responsivities of the APD1 and APD2 were calibrated using two fluorescent dyes with known QYs: DY-781-01 and DY-470, purchased from Dyomics and previously characterised according to IUPAC protocol[1]. For the APD1 calibration, the laser operating at a wavelength of 785 nm was utilised to excite the DY-781-01 dye. To ensure that the laser light would reach and excite the dye, the correct mirrors were flipped up, and appropriate spectral filters were placed in the optical slots in front of the APD to avoid stray light from the laser source. The 800 nm emission of the dye was measured at the APD1 for various excitation powers. Using the known QY of the dye, the wavelength-dependent responsivity of the APD1 was calibrated according to the emitted signal at the 800 nm emission from the dye. The same procedure was repeated for the calibration of the APD2 using the DY-470 dye excited with the laser operating at 405 nm. With this calibration, the voltage signals from the APDs can be easily converted to absolute units of power for UCL measurements at various wavelengths, accounting for the geometric factor caused by the small solid angle of detection.

2 Internal Quantum Yield

Table 1: iQY values for various excitation power densities. This table corresponds to a few values presented in the Fig. 4 in the paper.

Power density (W/cm^2)	iQY at 800 nm (%)	iQY at 650 nm (%)	iQY at 470 nm (%)
1.3e-02	3.3e-04	1.8e-09	3.4e-09
2.2e-02	5.7e-04	5.4e-09	1.0e-08
3.8e-02	1.0e-03	1.6e-08	3.2e-08
6.7e-02	1.7e-03	5.0e-08	9.6e-08
1.2e-01	3.0e-03	1.5e-07	2.9e-07
2.0e-01	5.3e-03	4.6e-07	8.9e-07
3.6e-01	9.2e-03	1.4e-06	2.7e-06
6.2e-01	1.6e-02	4.2e-06	8.2e-06
1.1e+00	2.7e-02	1.3e-05	2.5e-05
1.9e+00	4.6e-02	3.8e-05	7.3e-05
3.3e+00	7.8e-02	1.1e-04	2.1e-04
5.8e+00	1.3e-01	3.1e-04	6.0e-04
1.0e+01	2.0e-01	8.4e-04	1.6e-03
1.8e+01	2.9e-01	2.1e-03	4.2e-03
3.1e+01	3.9e-01	4.9e-03	9.8e-03
5.4e+01	5.0e-01	1.0e-02	2.1e-02
9.4e+01	5.9e-01	2.0e-02	4.0e-02
1.6e+02	6.6e-01	3.4e-02	6.8e-02
2.9e+02	7.0e-01	5.2e-02	1.1e-01
5.0e+02	7.3e-01	7.2e-02	1.5e-01

References

[1] C. Würth, M. Grabolle, J. Pauli, M. Spieles and U. Resch-Genger, *Nature Protocols*, 2013, **8**, 1535–1550.