Nitrogen-Doped Graphene Quantum Dots and Reduced Graphene Quantum Dots for Intensity Luminescence Nanothermometry

Ryan L. McKinney, Bong Han Lee, Tanvir Hasan, A. Naumov

Department of Physics and Astronomy, Texas Christian University

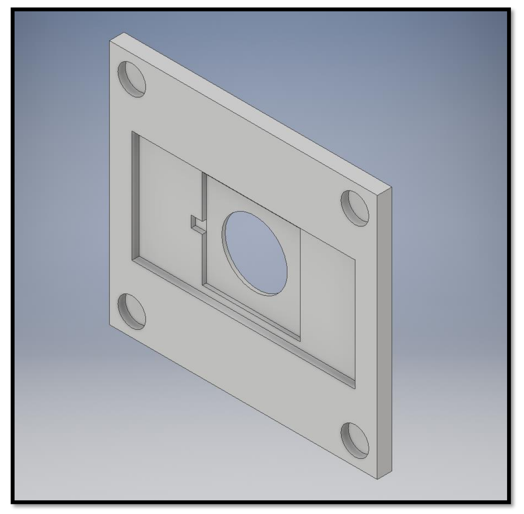
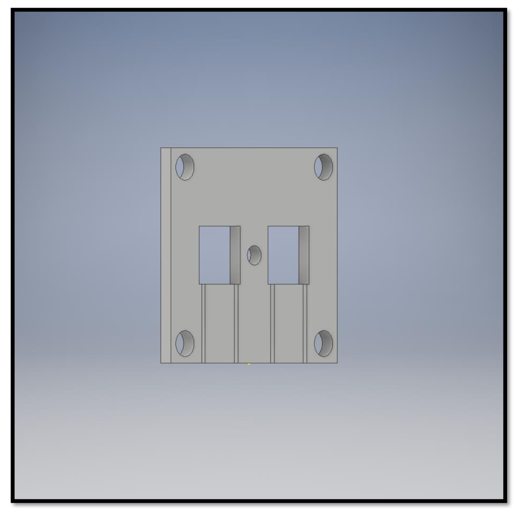
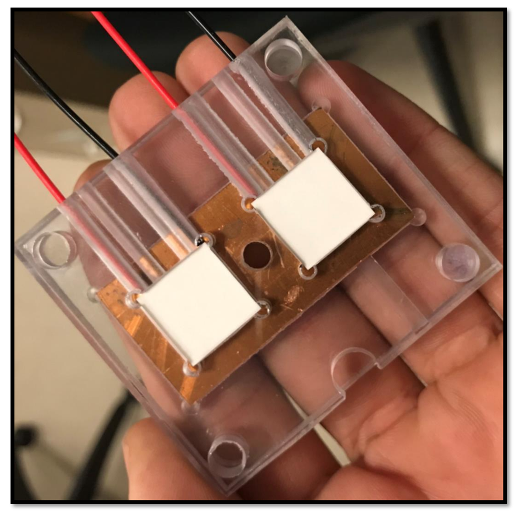
Abstract

Non-invasive temperature sensing is necessary for the analysis of biological processes occurring in the human body including cellular enzyme activity, protein expression, and ion regulation. Considering that a variety of such biological processes occur at the microscopic scale, a mechanism allowing for the detection of the temperature changes in microscopic environments is desired. Although several such techniques have been developed involving nanomaterials, there is still a need in deterministic non-invasive biocompatible approach allowing for temperature measurements both outside the cells and in the intracellular compartments. Here we develop a novel approach utilizing graphene quantum dots (GQDs) as agents for such detection. Because of their small 2-5 nm size, non-invasive optical sensitivity to temperature change and high biocompatibility, GQDs enable biologically safe sub-cellular resolution imaging. Both bottom-up synthesized nitrogen-doped graphene quantum dots and quantum dots produced from reduced graphene oxide via top-down approach in this work exhibit temperature-induced fluorescence variations used as sensing mechanism. Distinctive quenching of quantum dot fluorescence by up to 19.8 % is observed, in a temperature range from 25℃ to 49℃, in aqueous solution, while the intensity is restored to the original values as the temperature decreases back to 25℃. A similar trend is observed *in vitro* in HeLa cells as the cellular temperature is increased from 25℃ to 41℃. Our findings suggest that the temperature-dependent fluorescence quenching of bottom-up and top-down-synthesized graphene quantum dots can serve as non-invasive reversible deterministic mechanism for temperature sensing in microscopic sub-cellular biological environments.

Purpose

The purpose of this experiment is to explore the use of graphene quantum-dot derivatives as intracellular intensity luminescence nano-thermometers. Also, this experiment served to answer if the graphene quantum-dots displayed reversible photoluminescent quenching as intensity luminescence nano-thermometers.

Method

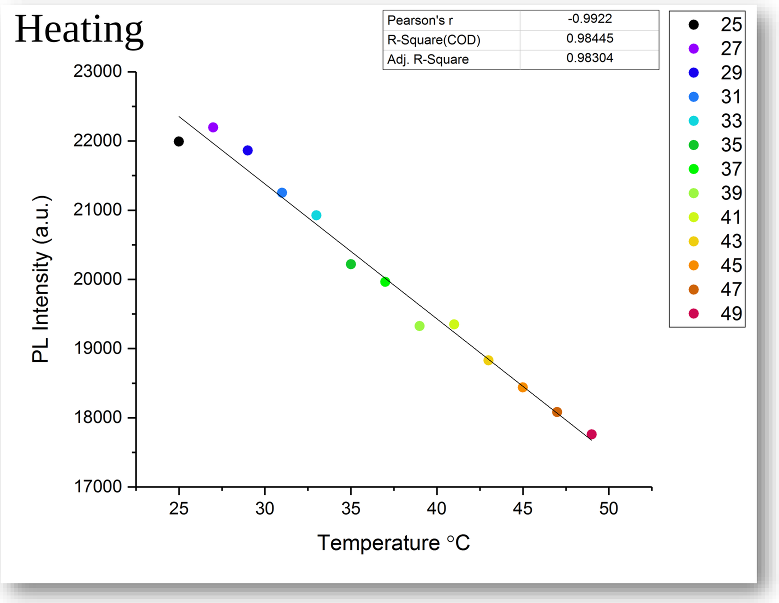
- Insulated Microscopy Thermal Device: Modeled with AutoDesk Pro. and engineered by TCU Engineering specialists.
- Thermoelectrical Peltier Modules were used as a heat source due to their compact size, heating rate, and controllability.
- Copper is used for its thermal conduction properties.
- Thermal paste adheres modules to copper surface.
- Cover slips, with sample sealed between them, are placed below copper.
- A thermistor is placed next to the cover slips—thermal paste adheres thermistor to copper.
- To control potential, a DC power supply is connected to the module.
- Thermocouple is used for temperature readings.

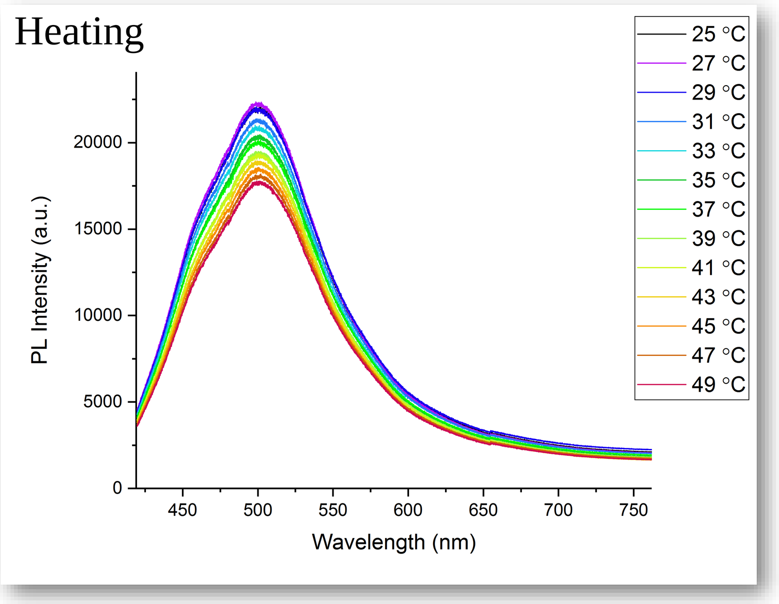
Findings

- Fluorescence decreases linearly with increase in temperature.
- Spectral shape is retained and quenching is reversible.
- UV-Vis GQD absorbance shows no temperature dependence.
- Near-infrared absorbance feature shows reversible increase with temperature.

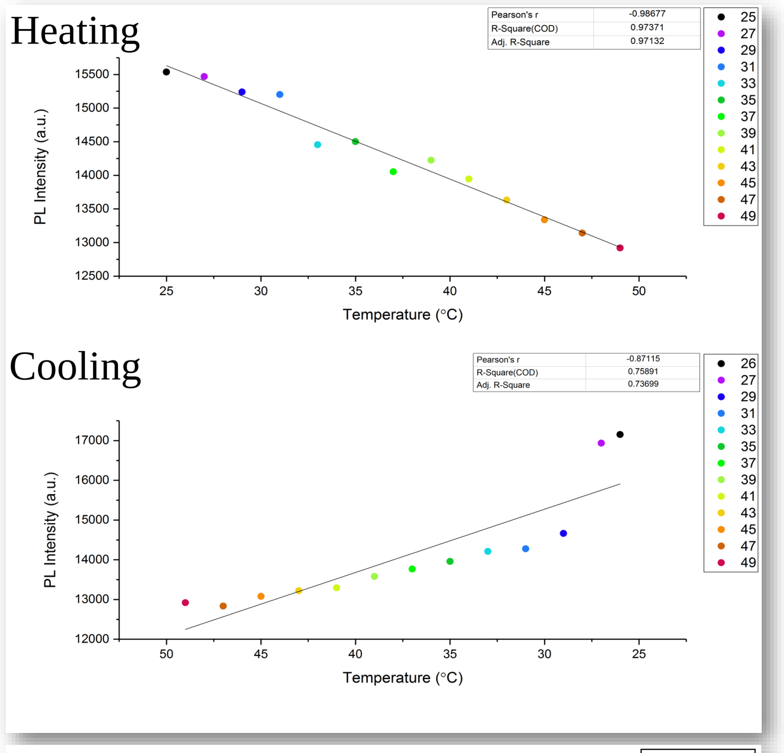
Graphical Data

N-GQD Visible Emission

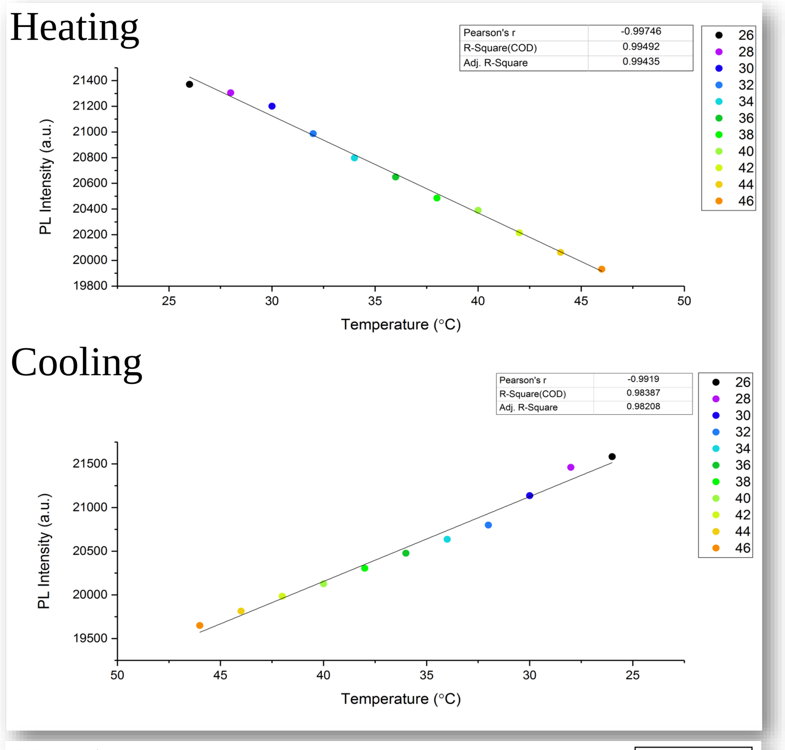


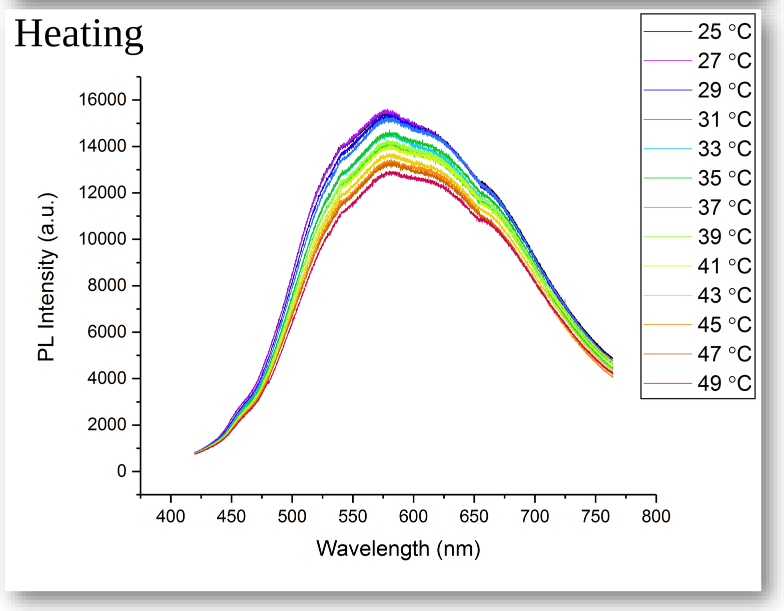


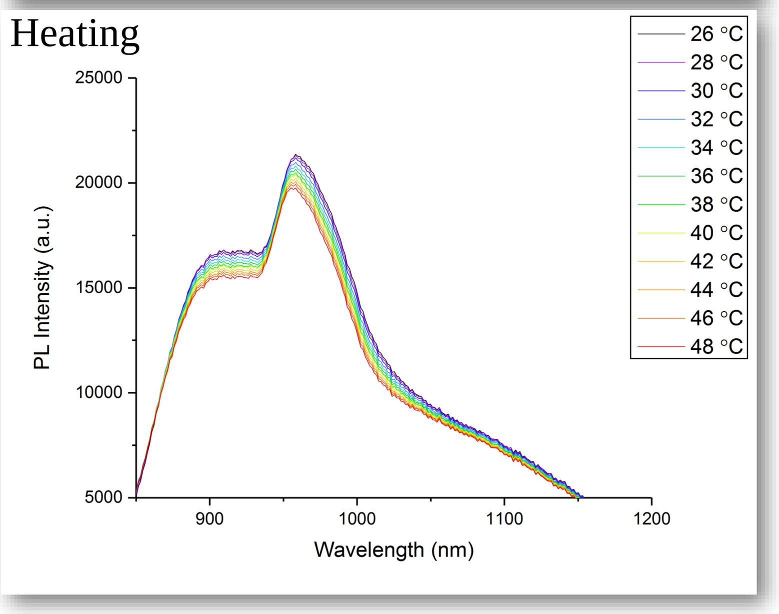
rGQD Visible Emission



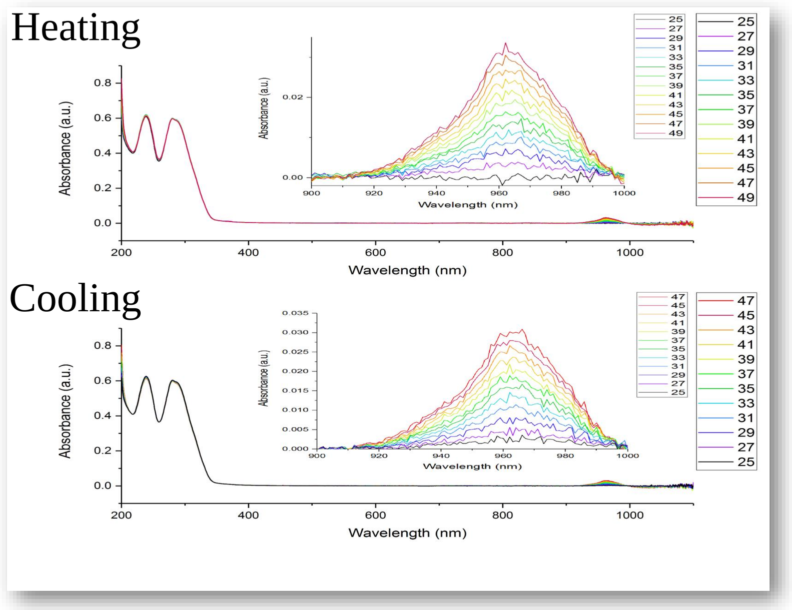
rGQD Near-Infrared Emission



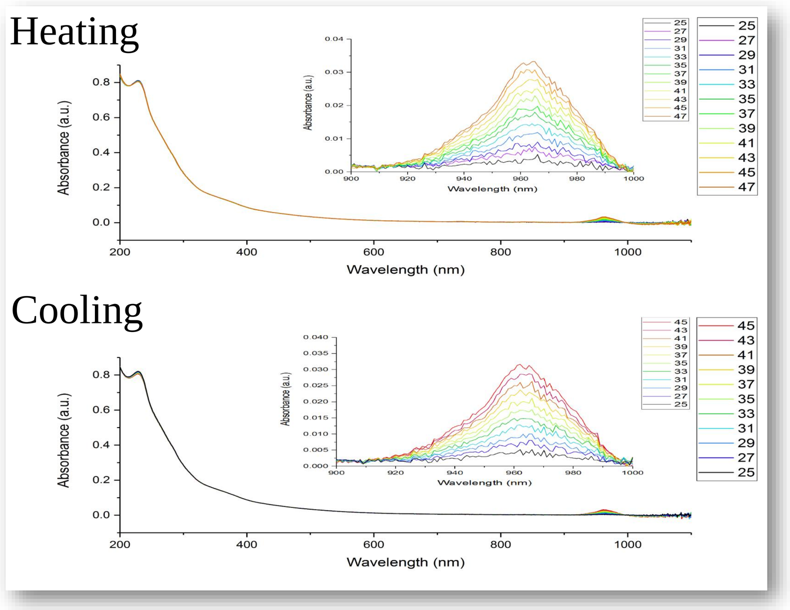




N-GQD Absorbance

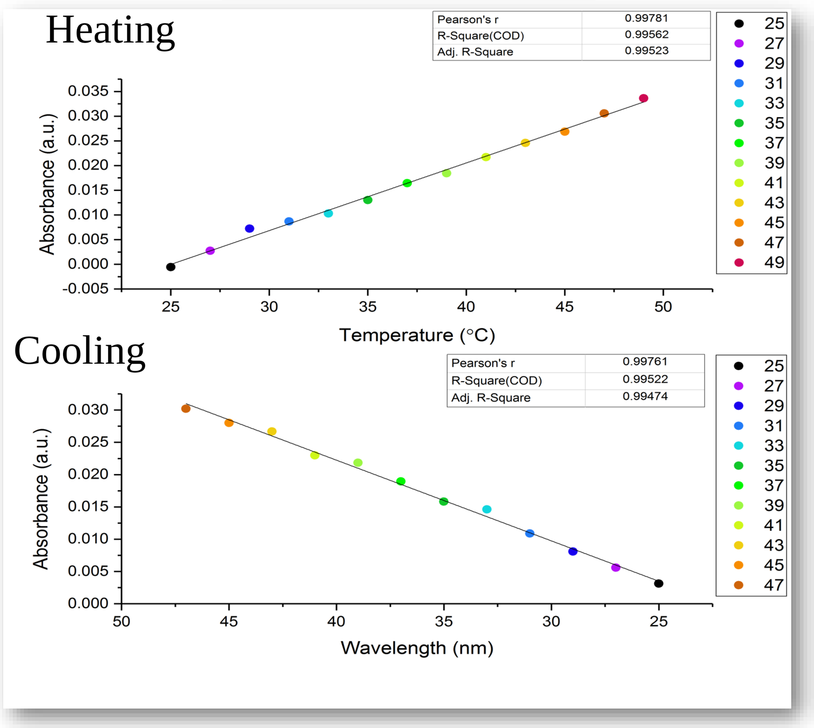


rGQD Absorbance

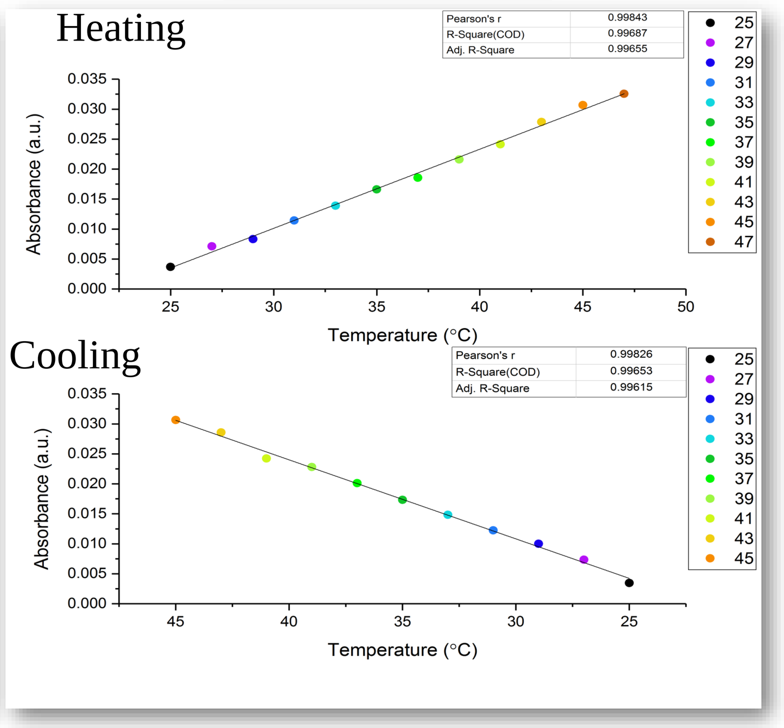


Graphical Data

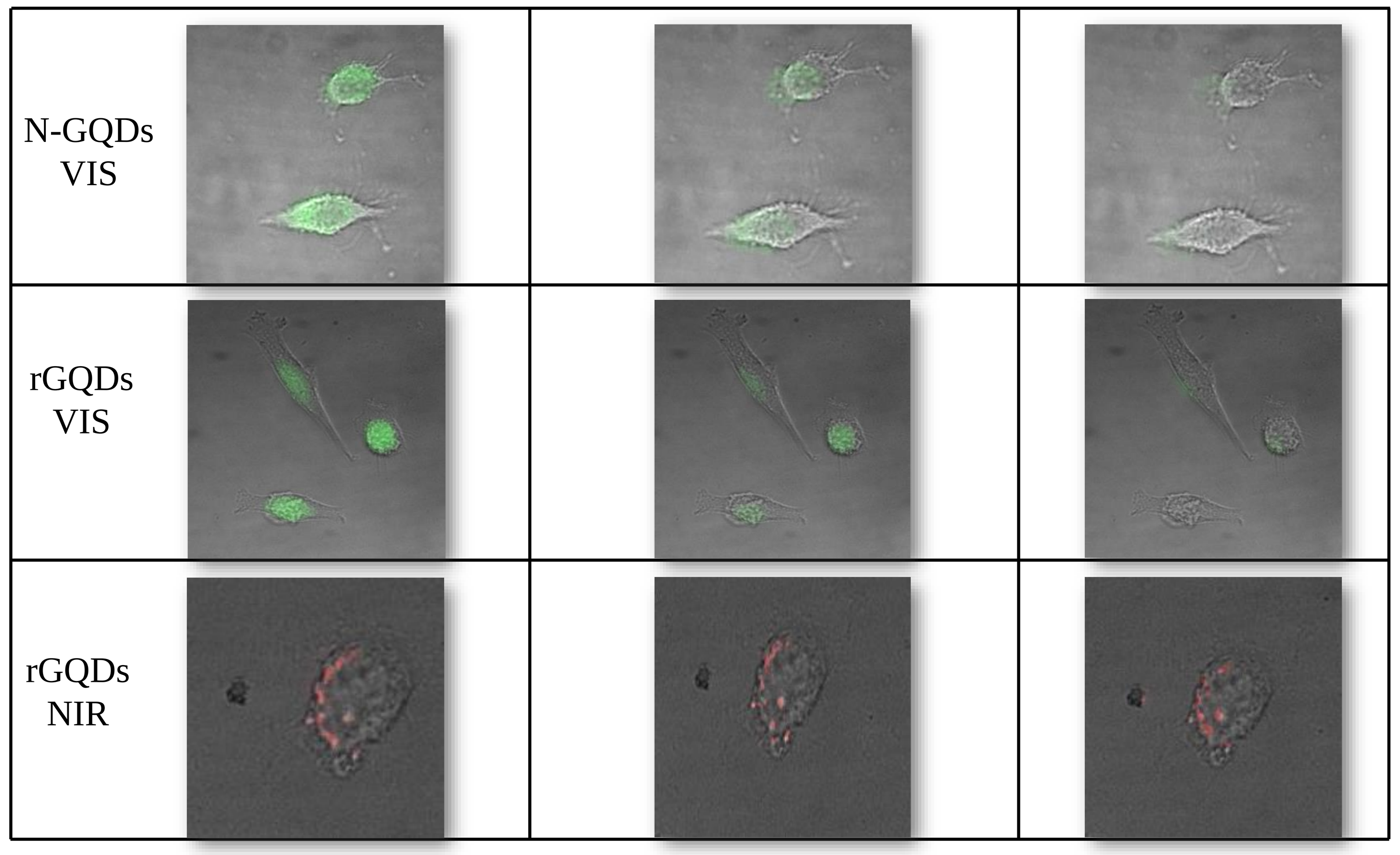
N-GQD Absorbance



rGQD Absorbance



Graphene Quantum Dots in HeLa Cells



25℃ 37℃ 45℃

Summary

- N-GQDs and rGQDs show fluorescence quenching as the temperature of the environment increases.
- Quenching is linear and reversible: temperature can be deduced from intensity.
- UV-Vis absorbance does not depend on temperature; NIR absorbance ~900 nm increases
- Near-infrared rGQD emission shows temperature dependence: potential for *in vivo* nanotermometry.
- Fluorescence/temperature dependence is retained *in vitro* in HeLa cells within biological temperature range.
- N-GQDs and rGQDs are promising intracellular imaging-based temperature sensors.