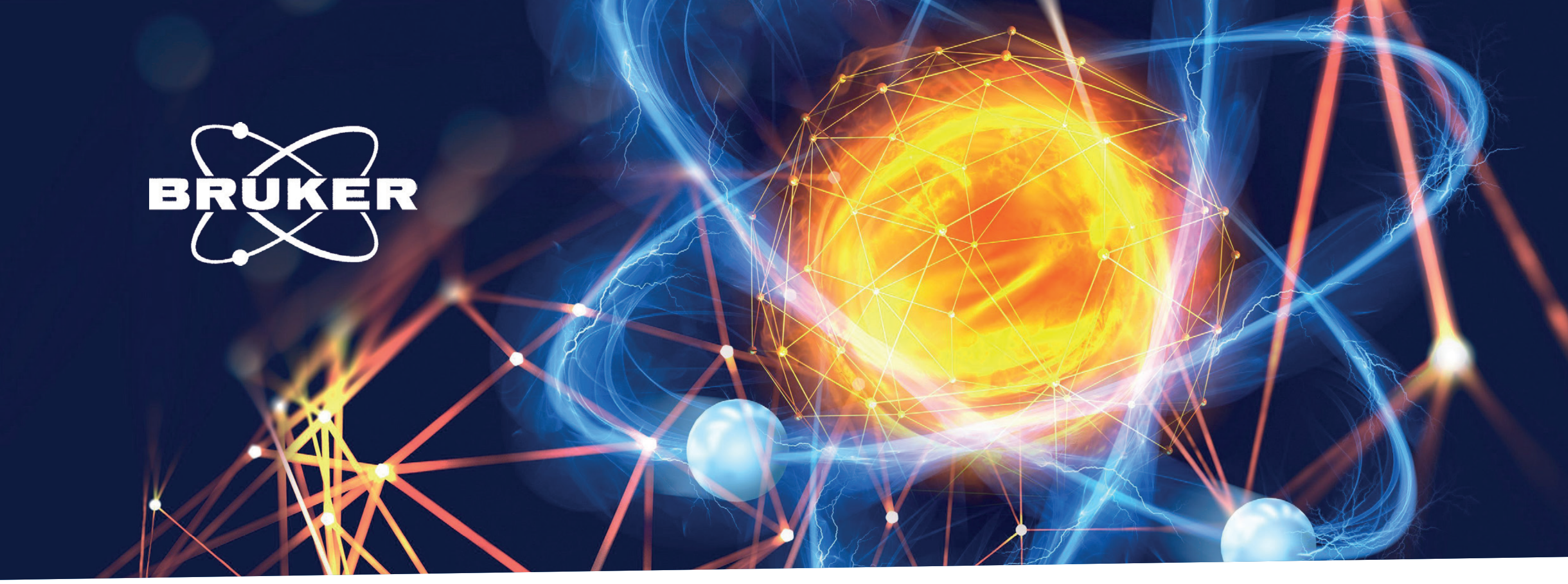


NIR and MIR Photoluminescence of Quantum Dots

Application Note M179

A little bit of history...

The history of quantum dots (QDs), tiny semiconductor particles at the nanoscale, is a tale of scientific discovery and technological innovation that began in the early 1980s. These tiny particles exhibit unique optical and electronic properties that have since found application across a range of fields.

In the early 80s Russian physicist Alexey Ekimov and American chemist Louis E. Brus independently embarked on research into semiconductor clusters. Ekimov explored Cadmium Selenide (CdSe) quantum dots, noticing that their optical properties changed with size. Meanwhile, Brus delved into colloidal semiconductor nanocrystals, demonstrating the quantum confinement effect, where nanoscale materials exhibit different electronic properties compared to their bulk counterparts. In 1993, Moungi Bawendi revolutionized the chemical production of quantum dots, resulting in almost perfect particles. This high quality was necessary for them to be utilized in applications [1].

Quantum dots came into practical use in the late 90s and early 2000s. They found applications in various fields, including biology, where they became essential for fluorescent labeling and precise tracking of biomolecules. Simultaneously, industries explored their potential in displays, photovoltaics, and even quantum dot-based lasers.

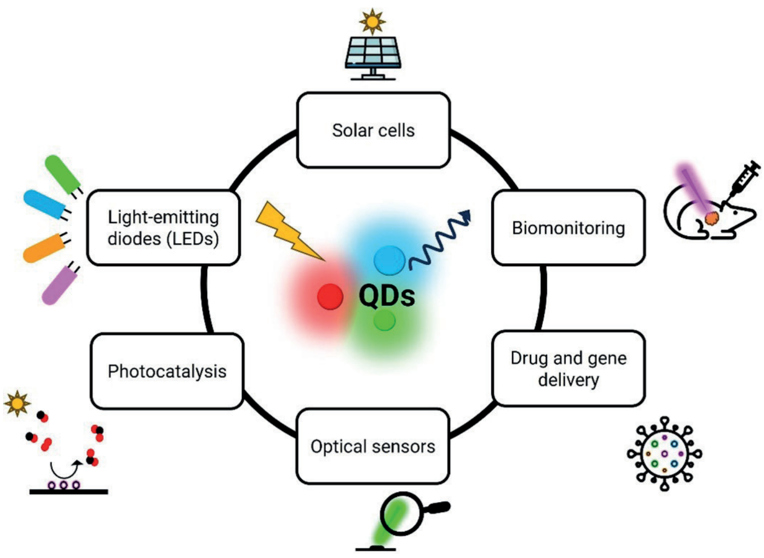


Fig. 1
Typical applications of quantum dots; based on [2].

Throughout the 2010s, quantum dot technologies continued to advance. In September 2015, Philips unveiled a computer monitor that achieved a brilliant color display using quantum dots. The Philips monitor was the first of its kind, following on the heels of the television that uses quantum dots to enhance its backlighting. Notably, QDs became integrated into displays, offering improved color accuracy and energy efficiency, particularly in high-quality LCD TVs and monitors. Since then, the term "quantum dots" became mainstream [3].

In 2023, The Royal Swedish Academy of Sciences acknowledged 35 years of QD technology development by awarding the Nobel Prize in Chemistry to Moungi G. Bawendi, Louis E. Brus, and Alexei I. Ekimov *"for the discovery and synthesis of quantum dots"*.

Understanding quantum dots...

Quantum dots are tiny crystals formed by growing or etching semiconductor materials, with sizes ranging from one nanometer to a few dozen nanometers. They typically consist of a relatively small number of atoms, typically between 1,000 to 100,000. This makes them large enough for practical laboratory use but small enough to display quantum behaviors like individual atoms, leading to quantized charge and energy levels [2].

When stimulating a quantum dot with electricity or light, electrons switch over to higher energy levels. Upon returning to their lowest energy state, quantum dots emit light. The wavelength of this emitted light depends on factors such as the crystal's size, composition, and shape. Smaller crystals emit light toward the blue end of the spectrum, while larger ones exhibit a noticeable shift towards the visible spectrum, near-infrared, and even further into the mid-infrared range [2]. The depiction of the general process of quantum dot emission is presented in Figure 2.

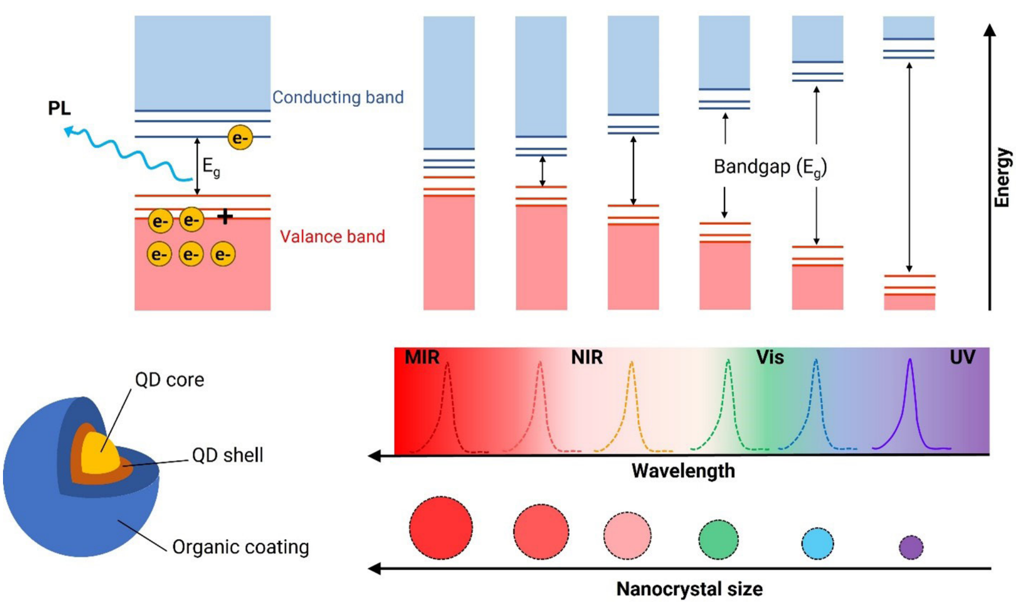


Fig. 2
The general process of QDs emission.

Quantum dots can be classified into different types based on their composition and structure. Generally, QDs can be classified as core type, core-shell type, and alloyed type [4].

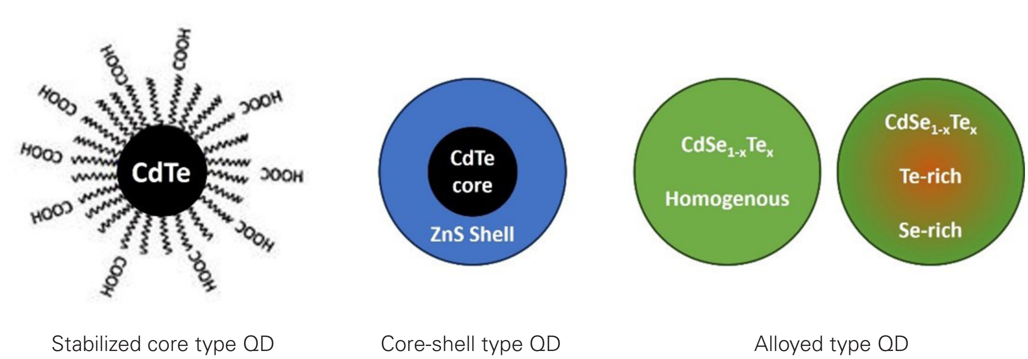


Fig. 3
Molecular structure of α-Lactose monohydrate.

QDs emitting in infrared

Quantum dots (QDs) that emit in the near-IR and mid-IR are important for a range of applications. NIR-emitting QDs are valuable in medical imaging, optical communication, and remote sensing, offering enhanced penetration and reduced tissue interference. MIR-emitting QDs have big potential for chemical sensing, thermal imaging, and advanced spectroscopy, allowing for precise detection and analysis of substances and enabling applications in security, defense, and environmental monitoring [2]. These QDs contribute to improving technology across diverse fields by expanding the capabilities of light-emitting devices. MIR-emitting LEDs are an in-demand technology expected to supplant blackbody light sources in various spectroscopic sensing and defense applications. This transition is driven by considerations of cost, power consumption, and practical aspects of usage , especially in cases where MIR lasers are not the most suitable choice [5].

FT-IR Photoluminescence measurements

FT-IR spectroscopy offers distinct benefits in the infrared spectral range compared to dispersive systems. The Jaquinot advantage enhances sensitivity in FT-IR spectrometers. Additionally, the Fellget advantage allows FT-IR to simultaneously achieve high spectral resolution and a wide spectral range in a single measurement. In contrast, dispersive systems usually trade high resolution for a narrower spectral range and may require grating changes. In FT-IR spectroscopy, spectral resolution is easily adjusted through software-controlled mirror movement. Furthermore, FT-IR instruments deliver superior spectral accuracy thanks to precise interferometer control lasers [6].

NIR PL measurements are relatively straightforward. However, mid-infrared measurements present additional challenges. The MIR range experiences more pronounced atmospheric absorption (e.g., water vapor and CO_2), and while reference measurements can compensate for atmospheric artifacts in techniques like reflectance or transmittance, PL measurements typically involve single-channel spectroscopy without such reference data. Moreover, in the mid-infrared, we are constantly surrounded by 300 K background radiation. High-gain liquid Nitrogen cooled detectors, used to capture weak MIR PL signals, are sensitive to this background radiation, which can mask the PL signals. As a result, MIR PL measurements demand more sophisticated solutions which are in detail described in application note AN 134 [7].

Bruker‘s Advanced Solutions for NIR and MIR PL

For NIR PL Bruker offers the versatile and comfortable PLII module (Figure 4(a), 6(a), and 6(b)). It can be attached to the right-hand side of VERTEX or INVENIO FT-IR R&D spectrometers equipped with suitable optical components to analyze PL [8]. Since in the NIR atmospheric absorption is rather weak, a vacuum spectrometer is not necessarily required when exclusively NIR PL measurements are performed.

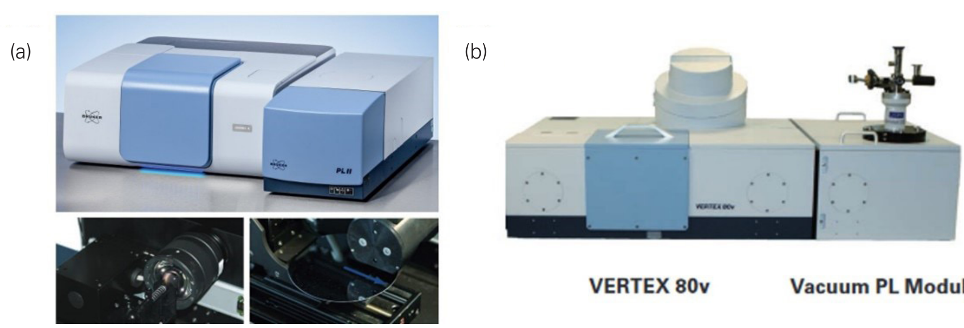


Fig. 4
(a) PLII module adapted to INVENIO FT-IR R&D spectrometer. Lower left-hand side: standard glass objective with vertical sample mount. Lower right-hand side: mirror objective and X-Y mapping stage for convenient horizontal sample positioning.
(b) VERTEX 80v with vacuum PL module and LHe flow through cryostat for low temperature MIR PL.

Drop casting is a relatively simple and cost-effective technique to fabricate quantum dots. It involves applying a droplet of QDs solution onto the glass, making it accessible even for researchers with limited resources or equipment. Drop casting on glass or Silicon a favorable method for subsequent photoluminescence studies of quantum dots. It allows for the uniform distribution of QDs on the surface. By controlling the concentration and dispersion of QDs in the solution, drop casting can help minimizing aggregation or clustering of QDs on the substrate.

Moreover, it has been shown that formation of 2D or 3D structures does not influence the PL signal [8]. The example results from the PL measurement of drop-casted PbS quantum dots in trichloroethane (TCE) solution on glass substrate obtained with PL II module and Vertex 80 FT-IR spectrometer are presented in Figure 5. The clear emission maximum from PbS QDs is visible at 6039 cm^{-1} (1657 nm). Compared to PL of PbS bulk material appearing at approx. 3300 cm^{-1} the PL signal of PbS QDs is significantly blueshifted by quantization effects. An additional peak at approx. 9000 cm^{-1} is originated from the glass substrate.

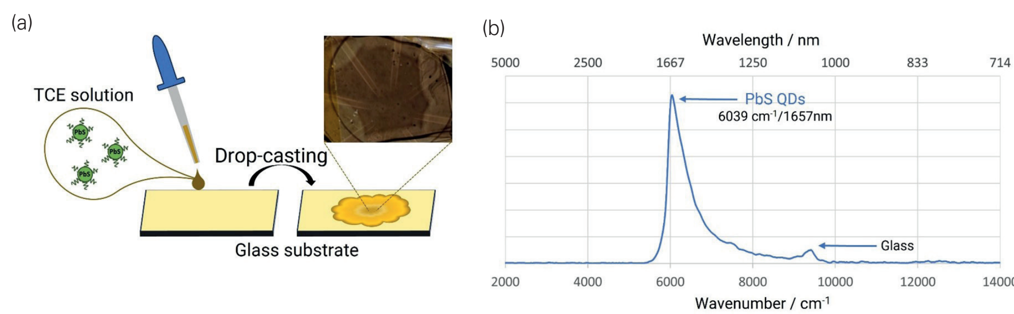


Fig. 5
Preparation of PbS QDs on the glass substrate **(a)** PL spectrum in the NIR region of PbS QDs deposited on the glass substrate **(b)** Spectrum was taken with 16 cm^{-1} resolution, 532nm CW, 80 mW excitation, and InGaAs detector; 16 scans were averaged.

As mentioned earlier, when conducting MIR PL measurements, more advanced methods are needed due to interference from atmospheric and thermal backgrounds. To avoid interference from water vapor and carbon dioxide, vacuum spectrometers like the VERTEX 70v or 80v are the perfect solution. For more information on the advantages of FT-IR measurements in vacuum please refer to our brochure [9].

To separate the weak MIR PL signals from the thermal background, one can use a simple trick: modulate the laser that excites the sample e.g., with a chopper wheel [10,11]. This modulation aligns with the PL signal and allows you to boost the signal while blocking out the constant thermal background. Since modulating the laser would interfere with the interferometer modulation, MIR PL experiments typically involve a step scan process. You can see the standard setup for these experiments in Figure 6(b).

For more details, you can refer to application note AN 134 or reach out to our experts.

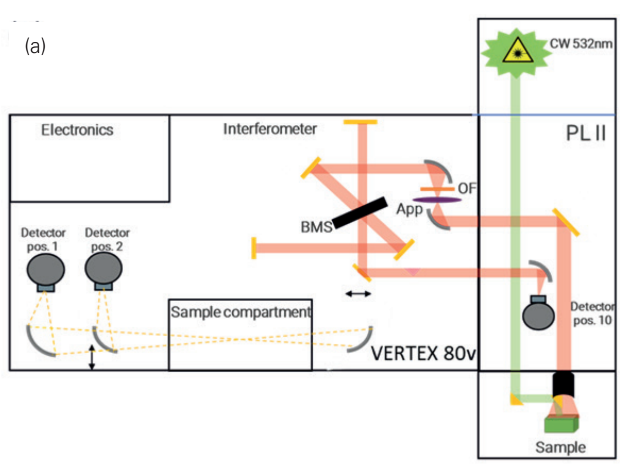
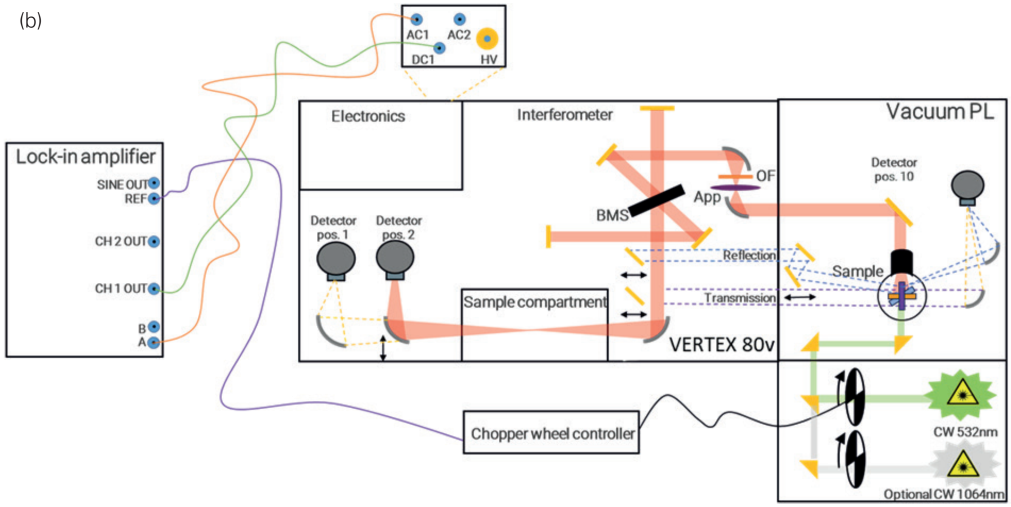


Fig. 6
Typical configuration for PL measurements including cable connections. **(a)** Standard NIR PL: measurements with PL II module and purged spectrometer. **(b)** Vacuum configuration for MIR PL measurement via amplitude modulated step scan.



Quantum dots have a strong reputation as highly promising materials suitable for both cryogenic (LN_2-cooled) and room-temperature (RT) mid-infrared detectors [12]. In Bruker's range of offerings, we provide multiple solutions not only for the analysis of detector materials but also for characterizing the completed detector devices. If you seek additional information, please consult our application note AN M161 [13].

Conclusions

Bruker offers an extensive array of solutions designed to facilitate the rapid, efficient, and trustworthy characterization of quantum dots, quantum dot materials, and quantum dot-based devices.

References

[1] https://nexdot.fr/en/history-of-quantum-dots/
[2] F. P. García de Arquer, D. V. Talapin, V. I. Klimov, Y. Arakawa, M. Bayer, E. H. Sargent, Semiconductor quantum dots: Technological progress and future challenges, Science 373, 640 (2021)
[3] S. Ornes, Quantum dots, PANS 113 (11) 2796 (2016)
[4] E. Munasinghe, M. Aththapaththu, L. Jayarathne, Magnetic and Quantum Dot Nanoparticles for Drug Delivery and Diagnostic Systems [in:] Colloid Science in Pharmaceutical Nanotechnology. IntechOpen. doi: 10.5772/intechopen.88611 (2020)
[5] A. A. Sergeev, D. V. Pavlov, A. A. Kuchmizhak, et al. Tailoring spontaneous infrared emission of HgTe quantum dots with laser-printed plasmonic arrays. Light Sci Appl 9, 16 (2020)
[6] P.R. Griffiths, "Fourier Transform Infrared Spectroscopy", 2nd edition, Wiley-Interscience (2007).
[7] Bruker application note AN 134
[8] V. A. Ermakov, J. M. C. da Silva Filho, L. G. Bonato et al. Three-Dimensional Superlattice of PbS Quantum Dots in Flakes, CS Omega, 3, 2027 (2018)
[9] Bruker Brochure: FT-IR Spectroscopy under vacuum.
[10] S. Sauvage et al., Midinfrared unipolar photoluminescence in InAs/GaAs self-assembled quantum dots, Phys. Rev. B, 60, 15589 (1999)
[11] J. Shao et al., Modulated photoluminescence spectroscopy with a step-scan Fourier transform infrared spectrometer, Rev. Sci. Instrum. 77, 063104 (2006)
[12] R. Chikkaraddy et al. Single-molecule mid-infrared spectroscopy and detection through vibrationally assisted luminescence. Nat. Photon. 17, 865–871 (2023)
[13] Bruker application note AN M161

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