# The Molecular Origin of Red Fluorescence in *o*-Phenylenediamine-based Carbon Dots

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Carbon dots (CDs) are a widely studied class of structurally diverse luminescent nanomaterials. The simplicity of their synthesis (especially via bottom-up methods using low-molecular-weight precursors) as well as their intense fluorescence (comparable to conventional organic dyes) makes them interesting for various applications, ranging from the development of fluorescent (bio)sensors for high-resolution fluorescence microscopy up to novel materials for optoelectronics. Despite huge efforts, their structure remains elusive, although it is known that the intense luminescence in as-prepared samples is to a large extent caused by free molecular fluorophores.

While most of CDs typically emit in the blue spectral region, red- or NIR-emitting systems are desirable for biological applications, because they can be excited with low-energy light within a so-called biological window, which penetrates into deep tissue layers and does not induce photodamage of the biological material. To prepare red-emitting CDs, traditionally used precursors (such as citric acid and various amines) were replaced by other, often nitrogen-containing reagents or additives, such as *o*-phenylenediamine (oPD), either alone or in combination with various dopants.

Upon closer examination of fluorescence data for various oPD-based red-emissive CDs reported in the literature, it can be noticed that although the procedures, dopants, and solvents differ from publication to publication, the emission maxima of CDs exhibit striking similarities, such as well-resolved vibrational structure of the emission bands and excitation-independent fluorescence behaviour. Yet they differ in the exact position of emission maxima (ranging from approx. 600 to 700 nm) and quantum yields (14-78%) [1]. The excitation-independent character of the fluorescence suggests the presence of a molecular fluorophore. In 2022, Bartolomei *et al*. [2] and Li *et al*. [3] independently analysed CDs prepared from oPD in an acidic environment under vastly different conditions employing solvothermal synthesis and pyrolysis, respectively, yet both of them identified the presence of the same red-emissive species, namely 5,14-dihydro-5,7,12,14-tetraazapentacene, also known as 5,14-dihydroquinoxalino[2,3-*b*]phenazine (DHQP). However, can the presence of a single organic molecular fluorophore explain the observed differences in emission maxima and PL quantum yields of all (or at least the majority of) oPD-based red-emissive CDs? In the talk, this question will be discussed from the perspective of available literature data and our synergistic experimental and theoretical endeavours.

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**REFERENCES**

[1] Tuchin V. S. at al., (2024) "Optical Properties Prediction for Red and Near-Infrared Emitting Carbon Dots Using Machine Learning". *Small*, 20, 2310402. DOI 10.1002/smll.202310402
[2] Bartolomei B. at al., (2022) "Nuclear Magnetic Resonance Reveals Molecular Species in Carbon Nanodot Samples Disclosing Flaws". *Angew. Chem. Int. Ed*., 61, e202200038. DOI 10.1002/anie.202200038
[3] Li P. at al., (2022) "Formation and fluorescent mechanism of red emissive carbon dots from o-phenylenediamine and catechol system". *Light. Sci. Appl.*, 11. DOI 10.1038/s41377-022-00984-5