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Lighting up the Electrochemiluminescence of Carbon Dots through Pre- and Post-Synthetic Design[1]

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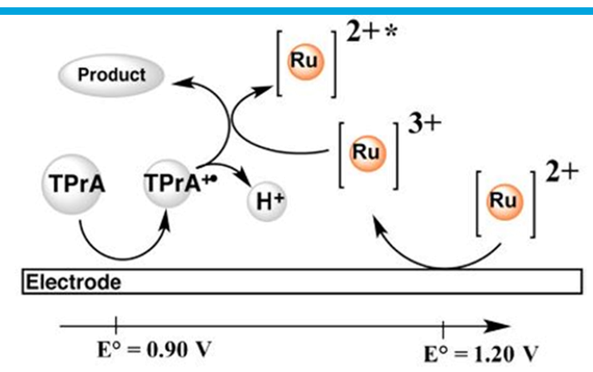
[1] Arcudi, F. *et al.* Lighting up the Electrochemiluminescence of Carbon Dots through Pre- and Post-Synthetic Design. *Adv. Sci.* 2100125, 2100125 (2021)

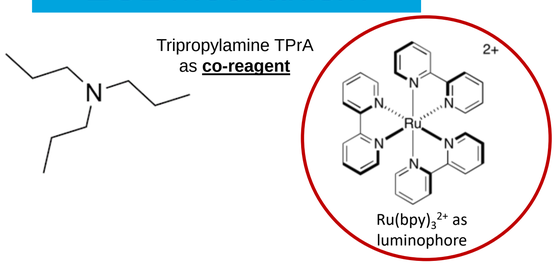
Electrochemiluminescence is a luminescent phenomenon induced by an electrochemical stimulus with a **high signal-to-noise ratio**. ECL has interesting features as low background, high sensitivity, versatility that makes it a **leading technique** in the field of **immunoassays-based biomarker detection and biosensors fabrication**.[2] Biomarkers are biological indicators with a key role in identifying human body function changes. Their quantitative detection is fundamental in clinical monitoring implementation and early screening of diseases.[3]
In order to electrochemically generated the excited state with "oxidative-reduction" mechanism, two different precursors, i.e. luminophore and co-reactant, are required. In the quest for ever-increasing sensitivities, ECL can ideally be **coupled to nanotechnology** to develop new systems and strategies for analyte determination even in very complex matrices.[4] Nanotechnologies can improve the sensitivity and sensibility of ECL technique thanks to their advantageous and tuneable properties.[5]
Herein, we investigate carbon nanodots (CNDs) doped with boron-dipyrromethene (BODIPY) as an alternative to $Ru(bpy)_3^{2+}$ luminophores.



Schematic representation of the ECL coreactant "oxidative-reduction" mechanism

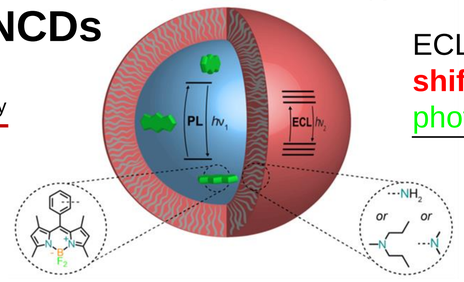
ECL Mechanism

Tripropylamine TPrA as **co-reagent**



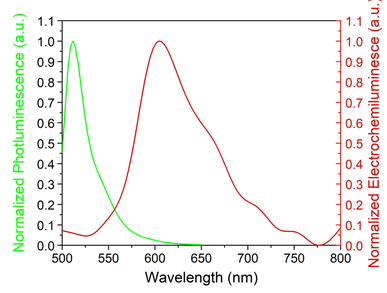
Here substituted by

carbon nanodots doped with boron-dipyrromethane
B-NCDs



ECL emission **red-shifted** respect to photoluminescent ones

Different excited states involved

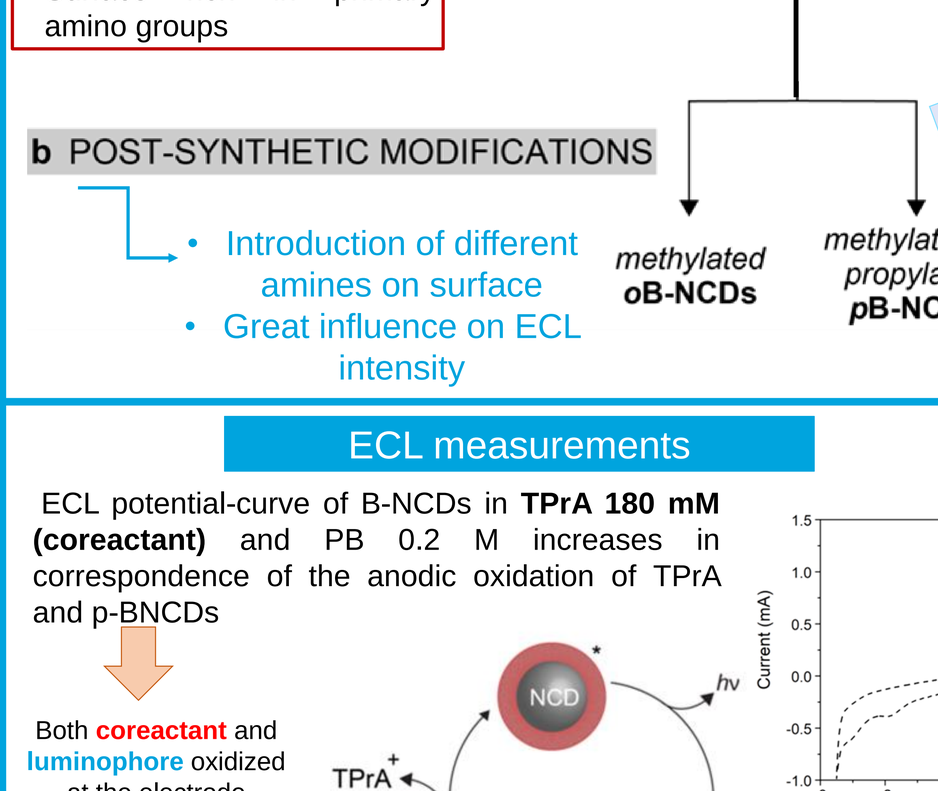


ECL signal has been recorded by a photomultiplier tube (PMT), with amplification at 750V, placed above the electrochemical cell put inside of a dark box and inserted in a dual-exit monochromator. The electrochemical cell is composed by glassy carbon as working electrode, Ag/AgCl as reference and Pt as counter electrode.

B-NCDS SYNTHESIS

New combination of two type of synthetic procedure is very important in order to create carbon dots with the molecular compound into the core and different types of ammine on the surface.

a PRE-SYNTHETIC DESIGN



Precursor for nitrogen doped carbon nanodots NCDs:
- Amorphous carbogenic core
- Surface rich in primary amino groups

Boron-dipyrromethene dye as PL and ECL active probe

b POST-SYNTHETIC MODIFICATIONS

- Introduction of different amines on surface
- Great influence on ECL intensity

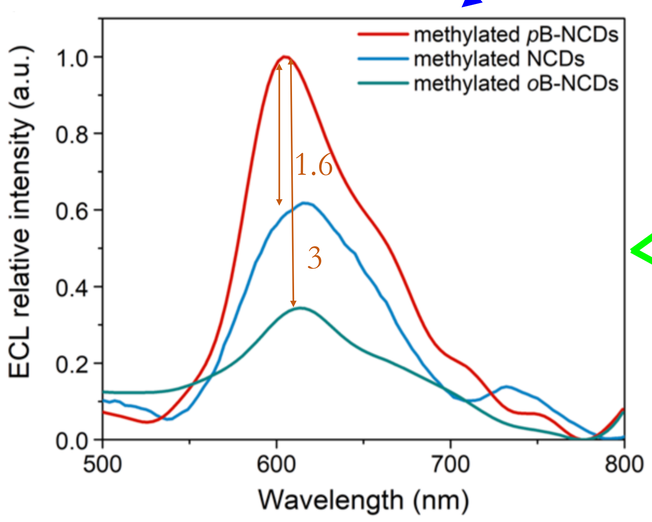
methylated **oB-NCDs**

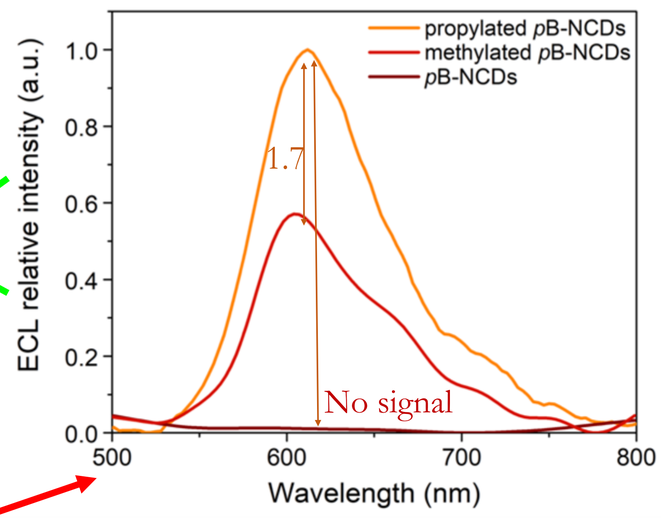
methylated or propylated **pB-NCDs**

Influence of B-NCNDs on ECL results

Proof of the correlation between the internal dye and the external superficial amine.

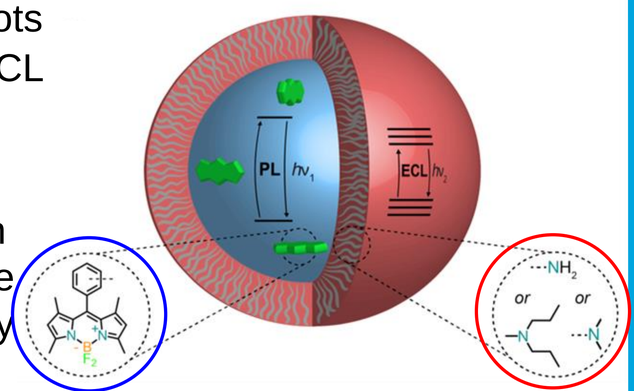
Effect of **BODIPY nanoenvironment** on ECL emission intensity is **lower** respect to the…





… effect of **surface properties** of carbon dots (different amino groups on the surface) on ECL emission intensity

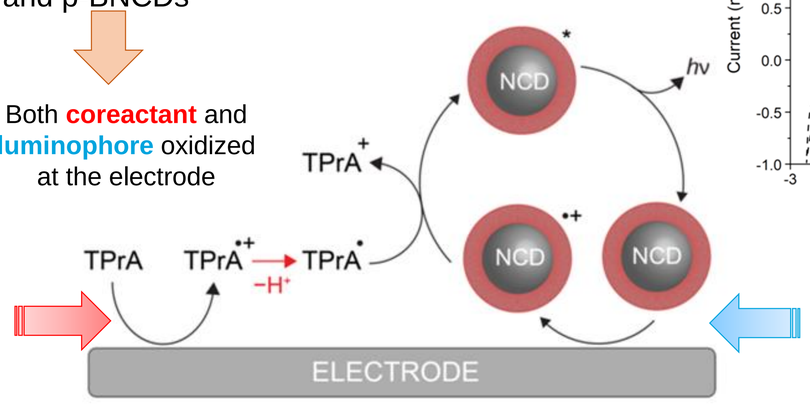
- Better stabilization of amine-centered radical cation
- Better alignment dye-doped core and surface states and consequent transfer of electronic density and stabilization

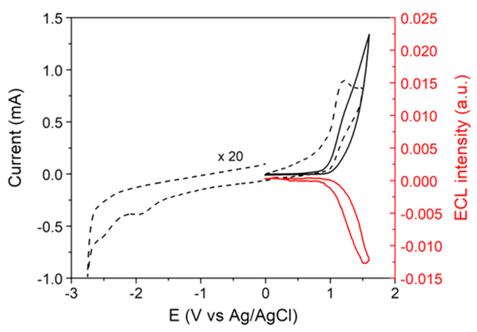


ECL measurements

ECL potential-curve of B-NCDs in **TPrA 180 mM (coreactant)** and PB 0.2 M increases in correspondence of the anodic oxidation of TPrA and p-BNCDs

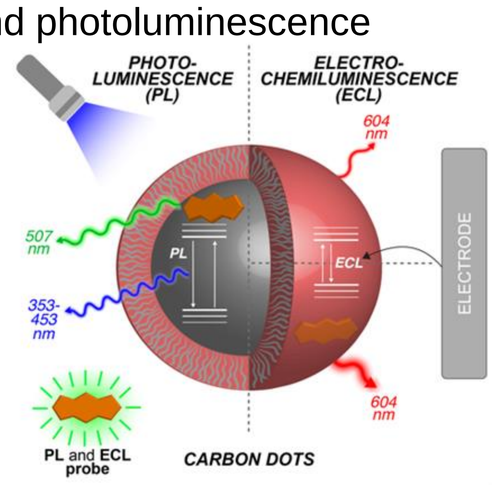
Both **coreactant** and **luminophore** oxidized at the electrode





CONCLUSIONS

- B-NCDs synthesized with a *pre- and post- synthetic method*.
- *Different excited states* involved in ECL and photoluminescence
- *ECL emission principally influenced by surface states* but with a little effect of BODIPY nano-environment
- Development of an efficient ECL nanomaterial
- **This study open new promising path towards more sensitive analyte detection, biosensing and point-of-care devices.**



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