EXTENDED ABSTRACT

Carbon Nanodot: Self-Assembly of Molecular Fluorophores and Potential Applications thereof

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Scope of the Thesis: The serendipitous observation of excitation-energy-dependent photoluminescence from nanoscale carbon particles in 2004 has rejuvenated the search for solution-processed, biocompatible, and photoluminescent carbon quantum dots. Even over a decade in pursuit of photoluminescent carbon quantum dot has created opportunities and left a huge void in its fundamental understanding. Their applications cover the most demanding areas of research in recent times, such as bioimaging, light-emitting diodes, hydrogen gas production, and green-fertilizers. The scope of the thesis to deepen our fundamental understanding of Carbon Nanodot and simultaneously explore potential applications. The questions that we choose to answer in this thesis are-

(i) Why does carbon nanodot exhibit excitation-(in)dependent emission?

(ii) What is the role of graphitic core in photoluminescence properties of carbon nanodot?

(iii) Is carbon nanodot an organic semiconductor or assembly of molecular fluorophores?

Chapter 1- *Introduction*: It contains a detailed literature survey on carbon nanodot covering studies in solution and solid states, in-vivo and in-silico as well. Emerging synthetic methods, photoluminescent properties have also been presented. Elemental-doping of carbon nanodot and emission tunability of doped nanodots have been elaborated. An emerging perspective of photoluminescent molecular self-assembly such as J-aggregate, H-aggregates for organic electronics have been outlined. Wide range of applications such as cell-imaging, biomedical, organocatalysis, light-emitting diodes, H_2 production, and CO_2 reduction have been illustrated.

Chapter 2- *Materials and Methodology*: It includes a list of chemicals used, various equipment employed, synthetic methods, and chromatographic separation, spectroscopic and microscopic characterizations. Experimental setup for flow chemistry, photocatalysis and time-correlated single photon counting have been included. Methods of spectroscopic and microscopic data analysis have been presented as well.

Chapter 3- *Connecting the Dots of Carbon Nanodot-Molecular Assembly*: In this chapter, solvent reactiveness has been found to manipulate the emission properties of the products derived from a one-pot solvothermal reaction. The excellent superimposition of absorption and excitation spectra and excitation-energy-independent emission of green- and red-emissive products are suggestive of their molecular nature. The best-known graphitic-N in the carbon nanodot turns out to be the nitrogen of citrazinic acid. The synthesized emitters exhibit reverse solvatochromism, surfactant-induced aggregation, and electrostatic sequestration at the micellar surface. An unprecedented solvent-directed green switching of the red-emissive

product (PR) has been presented here, and the transformed product (PR→G*) shows an uncanny resemblance of spectroscopic properties with the green-emissive product (PG). The products can easily bind to bovine serum albumin and retain their emissive properties in bound state, as signaled by the augmentation of fluorescence properties. Being a hybrid photosynthesis system, the chloroplast-red-emissive product is found to exhibit a markedly higher rate of reduction of ferricyanide than that of chloroplast alone.

Chapter 4- *Molecular Origin of Excitation-independent Emission of Carbon Nanodot*: In this chapter, a single-precursor approach has been adopted here for the synthesis of the yellow-fluorescent probe by using a bioresource, gallic acid. The synthesized probe exhibits excitation-energy-independent emission, a typical molecular behavior, but shows an emission-wavelength-dependent lifetime that is often attributed to the red-edge effect most commonly observed for nanodots. We propose here that the observation of the red-edge effect for a synthesized probe in neat solvents is due to proton-transfer controlled solvation, a unique photoprocess. Characterization and computational results of the synthesized product clearly suggest the formation of a molecular fluorophore. The presence of multiple phenolic-OH groups in the probe allows the easy formation of molecular chains of crystals on transmission electron microscopy grids, causing the observation of lattice spacing that remains unchanged in an aggregated state as well. We have also explored its possible applications in bioimaging and trivalent metal ion sensing. It has better cell-membrane permeability but remains predominantly in the cytoplasm. The product molecule possesses a submicromolar detection limit for aluminum ions as well, further confirming the unaltered position of phenolic-OH groups present in the product and substrate.

Chapter 5- *Scalable and Sustainable Photoluminescent Self-Assembly from Pyrogallol*:

In this chapter, the existing challenges in development of self-assembly based on π-conjugated molecules have been addressed– (i) feeble photoluminescence caused by poor molecular orientational ordering, (ii) costly fluorescent monomer owing to lack of atom/step/energy economical synthetic method. A bright yellow fluorescent Xanthene analog capable of instantly forming self-assembly can be synthesized by a home-build coil-in-spiral reactor using an inexpensive precursor, pyrogallol have been synthesized. Stimuli such as temperature (35^{o} C), acid fumes, and apolar solvent can trigger the formation of red-emissive self-assembly. In solution orientation of about 13 molecules yielding Hydrogen-bonded self-assembly has a direct resemblance with a Coulomb-coupled J-aggregate highlighted in the

Kasha model. In the solid state, the self-assembly retains the submicron-sized trigonal pyramidal structures by layer-by-layer stacking of triangular plates. This self-assembly doped in polymer even exhibits mechanofluorescence.

Chapter 6- *Chloroplast-based Hybrid Light Harvesting System for CO_2 reduction:* In this chapter, a green emissive fluorophore has been synthesized by using an industrial waste, fumaric acid. Scalable synthetic method using flow chemistry and one-pot solvothermal method have been tested for production of product with high yield. Spectroscopic characterization suggests its excellent photostability and surface functionalization ability. The synthesized fluorophore and chloroplast have been used to develop a hybrid light-harvesting system. A series of developed hybrid light-harvesting system have been tested for their ability to efficiently reduce CO_2 in presence and absence of metal ions.

Chapter 7- *Summary and Future Scope*: In this chapter results have been summarized and the future scope of the work has been outlined.

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