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Fluorescent carbon nanodots as efficient nitro aromatic sensor-analysis based on computational perspectives

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ABSTRACT

Herein, cyan emitting carbon dots are synthesised by adopting a facile, green and economic route using table sugar as the precursor. The system is adequately characterized by TEM, XRD, XPS, FTIR, Raman spectroscopy, Zeta potential analysis, UV–vis absorbance spectroscopy and Fluorescence spectroscopy. Excitation dependent emission is exhibited by these particles.The luminescence exhibited by these dots is found to be highly sensitive towards a collection of aromatic nitro compounds which enabled their sensing with admirable efficacy. Limits of detection towards the nitro aromatic systems are found to be in the range of 270–1720 Femto molar (fM), which is highly commendable while considering the benchmark values prescribed for the nitro aromaticsin aqueous systems, by the concerned authorities. The proposed carbon dot unit performed well even under complex chemical environments, as illustrated by the negligible interference of common metal salts and bio-moleculesin the sensing action. Besides, the observed sensing trend isscientifically corroborated with the aid ofwidely accepted computational analytical tools, Global reactive descriptors and Donor Acceptor Map (DAM) methods. Interpretation of sensing phenomena in a computational perspective is a novel attempt in the area of fluorimetric sensing, since works in the concerned area seldom seeks the assistance of a scientific MAP or parameter for explaining the sensing action.

1. Introduction

Carbon nanodots, the eco-friendly alternative to conventional semiconductor quantum dots,are receiving enormous amount of attention in recent time owing to their non-toxicity, higher solubility, commendable fluorescence intensity, tunable fluorescence emission, remarkable photo-stability and facile synthesis routes [1–7]. Carbon nanodots are defined as quasi spherical nano particles of carbon constituting amorphousto nano-crystalline frame work, decorated with plenty of functional groups including carboxyl, carbonyl and epoxy groups. They were first identified serendipitously during the preparative electrophoretic purification of single walled carbon nano tube, which triggered immense research interests in scientific community [8]. The characteristic feature of them, vis; the luminescence can be fine-tuned by means ofsurface passivation techniques, either during the course of the reaction or after the synthesis procedure [9,10]. Intense luminescence of these particles are exploited widely in areas like chemical sensing, bio-imaging, photo-catalysis and fabrication of optoelectronic devices [11–16,1,3,5,6].

The luminescent nature of carbon dots,a matter of debate, has been a matter of curiosity to the researchers [17–19]. Surface state, core-state/size confinement and molecular fluorescence [17,18] are the most accepted suggestions in this regard. This covetable optical property has bestowed them a prominent role in fluorimetric sensors, as any species potent enough to interfere the luminescence can be sensed using the system.Accordingly, their luminescence is well exploited for tracing out a number of chemical entities ranging from simple organic molecules to complex structural frameworks including charged and neutral analytes [6,12].

Herein, the carbon dots achieved from table sugar are well characterised, and the luminescent feature of the system in presence of some common nitrogen containing organic compounds is monitored. Molecules selected for the study included both aliphatic and aromatic nitrogen bearing compounds.Amines, amides, amino acids and aromatic/ aliphatic nitro compounds are used as analytes here. Interestingly, the system responded to nitro compounds only, specifically to aromatic nitro compounds, with high selectivity, enabling identification of these species from a group of nitrogen containing organic molecules. Nitro Aromatic compounds (NACs) are involved in the manufacture of insecticides, dyes, plastics,

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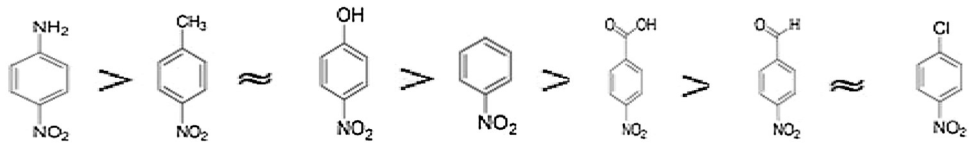

Fig. 8. Activity order of Nitro Aromatic Compounds combining global descriptive parameters and the DAM analysis results.

pounds 5–7 have electron releasing substituents. So, compounds 1–4 are electron deficient which in turn make them good electron acceptors and it follows the order p-Chloronitrobenzene > p-Nitrobenzaldehyde > p-Nitrobenzoic acid > p-Nitrobenzene. The electron releasing substituents make compounds 5–7 electron rich and good electron acceptors in the order p-Nitrophenol > p-Nitrotoluene > p-Nitroaniline.

Combining the global descriptive parameters and the DAM analysis results, all the seven tested NACs can be arranged in an order of activity as shown in Fig. 8, which is found to be in good agreement with the experimental results observed.

4. Conclusion

In summary, microwave irradiation of caramelized table sugar and ammonia mixture yielded bright cyan emitting carbon dots with fine features. The fluorescence emission of these carbon dots was exploited for the tracing of femto level concentrations of nitro aromatic compounds (NACs). The luminescence of carbon dots was quenched in presence of NACs including Nitrobenzene (NB), 4-Nitro aniline (4-NA), 4-Nitro Toluene (4-NT), 4-Nitro Phenol (4-NP), 4- Nitro Benzoic acid (4-NBA), 4-Nitro Benzaldehyde (4-NBAl) and 4-Chloro Nitrobenzene (4-CNB). The sensitivity of detection was in the order 4-NA>4-NT≈4-NP > NB> 4-NBA>4-NBAl>4-CNB. We have made a novel approach towards the sensing efficiency of carbon dots towardsNACs by analysing experimental data in computational perspective. For this, the observed quenching efficiencies of all the analytes were correlated with the global reactive descriptors and donor acceptor mapping (DAM), in order to frame the relation between the chemical reactivity of the analyte and its sensitiveness to structural perturbations and response to the changes in external conditions, which is a first attempt in fluorimetric sensing. Surprisingly, the experimental reactivity order of all NACs was in good agreement with the computational perspective, which is confirmed by their global reactive descriptors and the associated DAM plots.

CRediT authorship contribution statement

V.A Ansi: Conceptualization, Investigation. **K.R. Vijisha:** Resources, Investigation. **K. Muraleedharan:** Resources. **N.K. Renuka:** Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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