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Thermally Stable Crystalline Triazine-Based Organic Polymeric Nanodendrites for Mercury(2+) Ion Sensing

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Abstract : Organic polymers, constructed from light elements like carbon, hydrogen, nitrogen, oxygen, sulphur, and boron atoms, are the emergent class of non-toxic, metal-free, environmental benign advanced materials. Covalent triazine-based polymers with a functional triazine group are significant class of organic materials due to their remarkable stability arising out of strong covalent bonds. They can conventionally form hydrogen bonds, favour π–π contacts, and they were recently revealed to be involved in interesting anion–π interactions. The present work mainly focuses upon the development of a single-crystalline, highly cross-linked triazine-based nitrogen-rich organic polymer with nanodendritic morphology and significant thermal stability. The polymer has been synthesized through hydrothermal treatment of melamine and ethylene glycol resulting in cross-polymerization via condensation-polymerization reaction. The crystal structure of the polymer has been evaluated by employing Rietveld whole profile fitting method. The polymer has been found to be composed of monoclinic melamine having space group P21/a. A detailed insight into the chemical structure of the as synthesized polymer has been elucidated by Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopic analysis. X-Ray Photoelectron Spectroscopic (XPS) analysis has also been carried out for further understanding of the different types of linkages required to create the backbone of the polymer. The unique rod-like morphology of the triazine based polymer has been revealed from the images obtained from Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM). Interestingly, this polymer has been found to selectively detect mercury (Hg^{2+}) ions at an extremely low concentration through fluorescent quenching with detection limit as low as 0.03 ppb. The high toxicity of mercury ions (Hg^{2+}) arise from its strong affinity towards the sulphur atoms of biological building blocks. Even a trace quantity of this metal is dangerous for human health. Furthermore, owing to its small ionic radius and high solvation energy, Hg^{2+} ions remain encapsulated by water molecules making its detection a challenging task. There are some existing reports on fluorescent-based heavy metal ion sensors using covalent organic frameworks (COFs) but reports on mercury sensing using triazine based polymers are rather undeveloped. Thus, the importance of ultra-trace detection of Hg^{2+} ions with high level of selectivity and sensitivity has contemporary significance. A plausible sensing phenomenon by the polymer has been proposed to understand the applicability of the material as a potential sensor. The impressive sensitivity of the polymer sample towards Hg^{2+} is the very first report in the field of highly crystalline triazine based polymers (without the introduction of any sulphur groups or functionalization) towards mercury ion detection through photoluminescence quenching technique. This crystalline metal-free organic polymer being cheap, non-toxic and scalable has current relevance and could be a promising candidate for Hg^{2+} ion sensing at commercial level.

Keywords : fluorescence quenching , mercury ion sensing, single-crystalline, triazine-based polymer
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