



Graphene quantum dots coordinated to mercaptopyrindine-substituted phthalocyanines: Characterization and application as fluorescence “turn ON” nanoprobes



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ABSTRACT

This study reports on the design of novel nanoconjugates of graphene quantum dots (GQDs) and tetra or octa-mercaptopyrindine-substituted zinc and aluminium phthalocyanines (Pcs) deployed as fluorescence “turn ON” nanoprobes. The phthalocyanines were separately adsorbed onto the planar structure of graphene quantum dots (GQDs) via π - π stacking interaction to form GQDs-mercaptopyrindine Pcs nanoconjugates. The quaternized Pc complexes could also interact with the GQDs through electrostatic attraction due to the positive charges on the Pc ring substituents and the negative charges on the surface of GQDs. The fluorescence emission of the GQDs was quenched upon coordination to the respective Pcs. However, the fluorescence emission was “turned ON” in the presence of Hg^{2+} employed as a test analyte. The mechanism of the “turn ON” of the GQDs emission in the nanoconjugates is ascribed to the strong affinity of Hg^{2+} to bind with the bridging sulfur on the Pcs periphery thereby disrupting the π - π stacking interaction between the GQDs and the Pcs with a consequent “turn ON” of the coordinated GQDs’ fluorescence.

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1. Introduction

Graphene quantum dots (GQDs) are carbon-based nanomaterials characterized by tunable photoluminescence (PL), good electron donating abilities, robust chemical inertness, excellent photostability, high biocompatibility, low toxicity, and high solubility in aqueous and non-aqueous solvents [1,2]. GQDs have emerged as novel materials for the fabrication and design of nanosensors and are effective alternatives to semiconductor QDs [3]. GQDs have been employed in the detection of various target analytes ranging from metal ions, DNA, proteins, small organic molecules and biomaterials with comparatively better biocompatibility, sensitivity and selectivity than semiconductor QDs, metallic nanoparticles (Au and Ag) or carbon nanotubes [4]. The direct deployment of GQDs alone for analytes sensing generally involves the quenching (“turn OFF”) of GQDs fluorescence emission which is less reliable since the quenching may not be due to the analytes alone, thereby resulting in false positive signals. Conversely, fluorescence “turn ON” approach is specific and more reliable. The controlled functionalization of GQDs with biomolecules and macrocycles has resulted in improved photophysical and chemical properties, leading to various applications of GQDs such as in nanoprobe fabrication (mostly as “turn ON” sensors),

fluorescence imaging microscopy and photocatalysis [4–6]. In light of the above, the nanoconjugates of GQDs and macrocycles with extended π -conjugated systems such as phthalocyanines (Pcs) could considerably extend GQDs-based nanosensors fabrication. GQDs’ planar structure consisting of delocalized π electrons of graphene enables strong π - π interactions with other π -conjugated aromatic molecules [7]. The presence of carboxyl and hydroxyl groups on GQDs surface and edges enable covalent attachment, electrostatic interactions and hydrogen bonding with other suitable moieties [8]. The synthetic versatility and excellent optical properties of phthalocyanines and porphyrins (Pcs) [9,10] have motivated their deployment in the fabrication of multifunctional hybrid materials in ‘donor–acceptor’ supramolecular ensembles involving various carbon-based nanomaterials, QDs and metallic nanoparticles [11–13]. GQDs assembled with metalloporphyrins (similar in structure to phthalocyanines) have been deployed for hydrogen peroxide and glucose sensing via a fluorescence “turn ON” process [14]. The GQDs fluorescence emission was quenched by the metalloporphyrin and was ‘switched ON’ in the presence of hydrogen peroxide [14]. The quenching of GQDs fluorescence by ZnPc complexes upon coordination was reported as well by us, but the quenching was not used for analyte detection [15].

Despite the potential of GQDs, not much is known about their conjugates with macrocycles possessing excellent electronic and optical properties such as phthalocyanines and porphyrins, hence limited

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