



A novel sensitive and selective nanocomposite sensor for Doxorubicin based on Graphene Oxide and fluorescent [2]Rotaxane



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ABSTRACT

Graphene oxide (GO) displays advantageous characteristics as a quencher due to its excellent quenching capacity toward organic fluorescent molecules. In this paper, GO is used as a quencher of RhBPy [2]rotaxane based on the mechanism of fluorescence resonance energy transfer (FRET), and a GO-based fluorescent probe that allows rapid, sensitive and selective detection of doxorubicin (DOX) in a MeOH/H₂O solution is reported. The results show that the efficient fluorescence quenching that occurs between GO and RhBPy [2]rotaxane is due to their strong noncovalent interactions via energy transfer, leading to very weak emission in the absence of DOX, while a strong red fluorescence is observed upon the addition of DOX into the RhBPy-GO solution. As a consequence, it is possible to employ the RhBPy-GO platform in DOX detection with high sensitivity and selectivity by monitoring changes in the fluorescence intensity of the MeOH/H₂O (3:2, v: v) solution.

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1. Introduction

Graphene oxide (GO) is a new type of carbon nanostructure material [1–5] that has stimulated great interest in recent years in many fields, including molecular sensors, drug delivery, photovoltaic cells, nanoelectronic devices and transparent conductors [6–10], because of its fluorescence quenching ability, biocompatibility, and extraordinary electronic, optical and thermal properties [11–14]. To date, GO has become one of the most widely studied carbon materials and has been frequently employed as an efficient quencher for organic fluorescent molecules because of its high quenching capacity [15–17]. A promising application of GO in molecular sensing is fluorescence detection based on fluorescence resonance energy transfer (FRET). This principle is recognized as a sensitive and reliable analytical procedure and has been extensively employed for analytical, biophysical and imaging purposes [18]. Great attention has been paid to the use of fluorescence donors with fluorescent dyes that use fluorescence quenchers as energy acceptors during the development of GO-based sensors for DNA, protein, glucose and metal ions [19–22]. For example, Huangxian Ju et al.

designed a novel platform for the effective sensing of biomolecules by FRET via the use of quantum dots of GO [23]. Seok Seo et al. discussed the fluorescence resonance energy transfer efficiency between GO and Cy3.5 dye by controlling the donor-acceptor distance using double-stranded DNA and demonstrated that the GO serves as an acceptor rather than a donor in this FRET system [24].

Rotaxane, a typical interlocked supramolecular system [25,26], is described as a molecular system in which the macrocycle interlocks with a dumbbell structure by noncovalent interaction [27–29], i.e., two bulky stoppers at the end of the axle are prepared to prevent dethreading of the cyclic component [30,31]. Because of their unique structural architectures, some supramolecular rotaxanes display increasing potential for use in applications such as molecular switches, molecular logic gates, molecular wires, and information storage [32–35]. However, few rotaxanes, especially fluorescent rotaxanes, have been developed as fluorescence sensors for small molecule detection. Therefore, research on the use of rotaxane-based fluorescent sensors for the rapid and simple detection of some special molecules is currently of increasing importance [36].

We have previously successfully synthesized a new RhBPy [2]rotaxane (Fig. 1) that contains dibenzo-24-crown-8 (DB24C8) rings interlocked through a dumbbell-shaped component with Rhodamine B pyrene moieties as the bulky stopper units [37]. Moreover, the results demonstrated that the RhBPy [2]rotaxane

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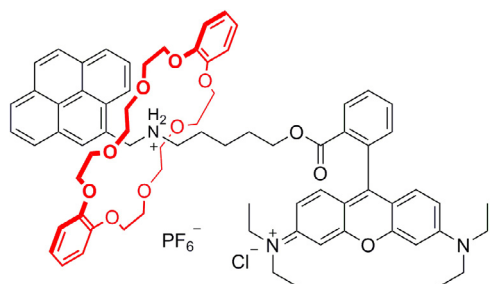


Fig. 1. The chemical structure of the as-synthesized RhBPy [2]rotaxane.

showed strong fluorescence due to the ring-opened ester form of the Rhodamine B unit of the rotaxane. Because of its large cavity and the strong electronegativity of oxygen atoms, the DB24C8 ring (consisting simply of a cyclic array of linked ether oxygen atoms) can associate with certain molecules via hydrogen bond interactions. Furthermore, the conjugated structure of the pyrene unit in RhBPy [2]rotaxane makes it easier to adsorb onto the surface of carbon materials through π - π interactions [38,39]. Inspired by the quenching of GO, we present a novel highly sensitive and selective fluorescence sensor (RhBPy-GO) using water-soluble GO and as-synthesized RhBPy [2]rotaxane as the fluorescence quencher and fluorescent dots, respectively. The results reveal that the proximity of GO to the pyrene moiety of RhBPy [2]rotaxane via π - π interactions and hydrogen bonding effectively quenches the fluorescence of the ring-opened Rhodamine B unit of RhBPy [2]rotaxane via FRET. We use this sensor to detect various antibiotics and find that the competitive binding of doxorubicin (DOX) with RhBPy [2]rotaxane results in the desorption of the pyrene-labeled rotaxane from the surface of GO upon the addition of DOX into the solution. DOX is an effective anthracycline used for treating various types of cancer with annually increasing global usage, especially in China. The monitoring of DOX is therefore attracting greater global attention [40,41]. Herein, a novel fluorescent sensor platform is developed to detect DOX with excellent sensitivity and selectivity using GO and RhBPy [2]rotaxane in a MeOH/H₂O solution (3:2, v:v).

2. Experimental procedure

2.1. Material and general methods

All reagents and organic solvents were ACS grade or higher and used without further purification. Unless otherwise noted, all chemicals were purchased from J&K Scientific (Shanghai, China). Reactions were performed under argon atmosphere with standard Schlenk techniques. The Fourier transform infrared spectra (FTIR) were measured with a Shimadzu FTIR-8400 S spectrometer using a thin KBr pill at a resolution of 2 cm⁻¹, over a wavenumber range of 400–4000 cm⁻¹. The morphology of the samples was analyzed by transmission electron microscopy (TEM, JEOL 2100). UV-vis and fluorescence spectra were obtained using a UV-3600 UV-VIS-NIR spectrophotometer (Shimadzu, Japan) and an Edinburgh FLS920 fluorescence spectrophotometer (Livingston, UK), respectively, at room temperature.

2.2. The preparation of GO and RhBPy [2]rotaxane

GO was synthesized according to a modified Hummers' method [42,43]. Then, the as-prepared GO was exfoliated in deionized water under sonication for approximately 2 h to give an aqueous solution of GO, after which the solution was centrifuged at 7000 rpm for 15 min to remove the non-exfoliated graphite oxide. The top supernatant GO solution was measured at 0.97 mg/mL for use in

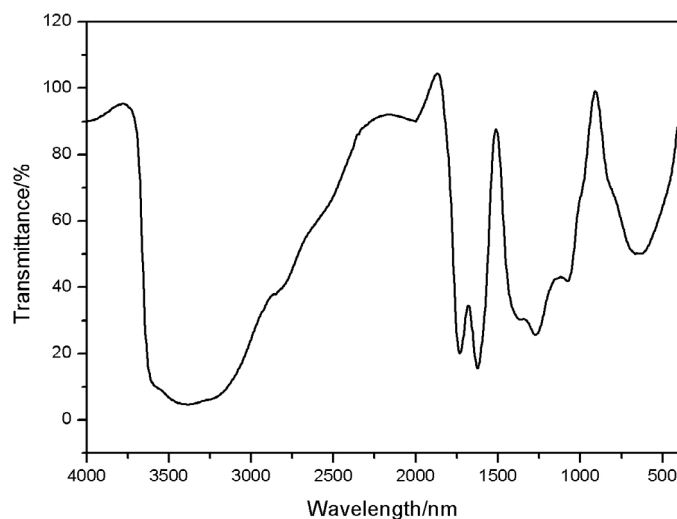


Fig. 2. The FTIR spectrum of exfoliated GO.

the following experiment. The RhBPy [2]rotaxane was synthesized according to our previous reports [37].

2.3. Stock solution preparation and spectral detection

Stock solutions of the antibiotics (Ampicillin (Amp), Chloramphenicol (Cm), Erythromycin (Em), spectinomycin (Spe), Gentamicin (Ga), Kanamycin (Kana), and Doxorubicin (DOX)) in water were prepared (the chemical structures of the antibiotics are shown in Fig. S1 in the ESI). The stock solution of RhBPy [2]rotaxane (1 mM) was prepared in MeOH/H₂O (3:2, v:v) solution. Working solutions of RhBPy [2]rotaxane and GO were freshly prepared by diluting the highly concentrated stock solution to the desired concentration prior to spectroscopic measurements.

For each spectroscopic measurement, 3 mL of the MeOH/H₂O solution was added to a quartz cell with 1 cm optical path length. Then, RhBPy [2]rotaxane, GO aqueous solution and a different antibiotic stock solution were gradually added into the quartz cell via micro-pipet. The mole ratio of the various antibiotics and RhBPy [2]rotaxane was 2:1. All spectroscopic measurements were performed at room temperature. All fluorescence measurements were taken with an excitation wavelength at 526 nm, and the emission range collected from 536 nm to 700 nm.

3. Results and discussion

3.1. The characterization of the GO sheets

FTIR spectroscopy is employed to investigate the functional groups of exfoliated GO. Fig. 2 shows a typical FTIR spectrum of oxidized carbon material, indicating exfoliated GO by the broad and intense peak of O-H groups centered at 3405 cm⁻¹, the strong C=O peak at 1734 cm⁻¹, the O-H deformation peak at 1392 cm⁻¹, the C-OH stretching peak at 1273 cm⁻¹, and the C-O stretching peak at 1074 cm⁻¹. The peak at 1625 cm⁻¹ is assigned to the vibrations of the adsorbed water molecules and also to the contributions from the skeletal vibrations of unoxidized domains in the GO. This spectrum confirms the successful oxidation of graphite. The TEM image of the as-prepared GO can be seen in Fig. 3. The GO sheets present a characteristic crumpled surface and show partially overlapped morphology, an indication of thickness of only a few layers. These crumpled, thick sheet structures can greatly increase the surface area. Taken together, these data support the premise that thick GO sheets were successfully prepared.

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