Research Article

A Turn-On Fluorescent Sensor for Hg^{2+} Based on Graphene Oxide

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A graphene oxide- (GO-) boradiazaindacenes (BODIPY) charge-transfer complex **(BGO)** has been easily synthesized, and the structure of **BGO** was confirmed by FT-IR and atomic force microscopy (AFM). Moreover, the **BGO** was found that could be used as a turn-on fluorescent sensor for Hg^{2+}. Upon addition of Hg^{2+}, the fluorescence of **BGO** would be enhanced since the energy transfer between BODIPY and GO was inhibited. The selectivity and the competition performance of **BGO** towards Hg^{2+} were good among other heavy metal ions.

1. Introduction

Most heavy metal ions are very toxic and pose risks to human health and environment. Among the metal ions, Hg^{2+} is one of the most dangerous toxic metal ions, which leads to many health problems including digestive, cardiac, kidney, and especially neurological diseases [1, 2]. Thus, development of specific and facile method for detecting Hg^{2+} in environment is highly desirable [3]. Among the well-known analytical methods, fluorescent sensors have received intense interests owing to their potential promises to on-site and real-time detection of toxic metal ions with low detection limits [1, 3]. Therefore, a lot of fluorescent sensors based on small molecules for monitoring Hg^{2+} have been reported [4]. Moreover, the chemists prefer to use organic-inorganic materials instead of organic dye as report part for fluorescent sensor [5]. The receptor-immobilized inorganic materials have some important advantages [6], such as being free from the pollution of organic molecules, easily recyclable, applicable in heterogeneous solid-liquid phase.

GO nanosheet, a two-dimensional oxidized derivative of graphene, also contains isolated polyaromatic clusters and can be easily exfoliated from graphite with a high yield under simple oxidizing conditions. It has been widely studied in regard to electrical conductivity, drug delivery, self-assembly, surface functionalization [7], and the application in optical sensor [8]. Usually, GO could act as a fluorescence quencher due to the energy transfer in the sensing system. However, it needs multiple steps to build up GO-based sensors [8].

BODIPY are very attractive functional groups for construction of molecular sensors because of their advantageous characteristics, such as sharp absorption and fluorescence bands, high extinction coefficients, high fluorescence quantum yields, and high stability against light and chemical reactions [9, 10]. Stankovich et al. reported synthesis of isocyanate-treated GO which is stable in polar aprotic solvents such as DMF and DMSO [11]. Herein, a chemically modified GO derivative **BGO** via treatment of GO with 4,4-difluoro-8-(4-isothiocyanatophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene **(BODIPY 1)** was synthesized in one step, and its application for selective sensing Hg^{2+} was also studied (Scheme 1).

2. Materials and Methods

The compound **BODIPY 1** was synthesized similarly as the reported reference [12]. In a round-bottomed flask, a solution of thiophosgene (0.04 mL, 0.56 mmol) in distilled CH$_2$Cl$_2$ (5 mL) was added dropwise to a solution of **1** [13] (0.1 g, 0.3 mmol) in anhydrous CH$_2$Cl$_2$/NEt$_3$ (20 mL/0.2 mL) under argon at 0°C. As soon as total consumption of the starting material was observed by TLC (one spot, about 5 min), the reaction was quenched with water (10 mL). The organic layer was then washed with water (3 × 20 mL), dried
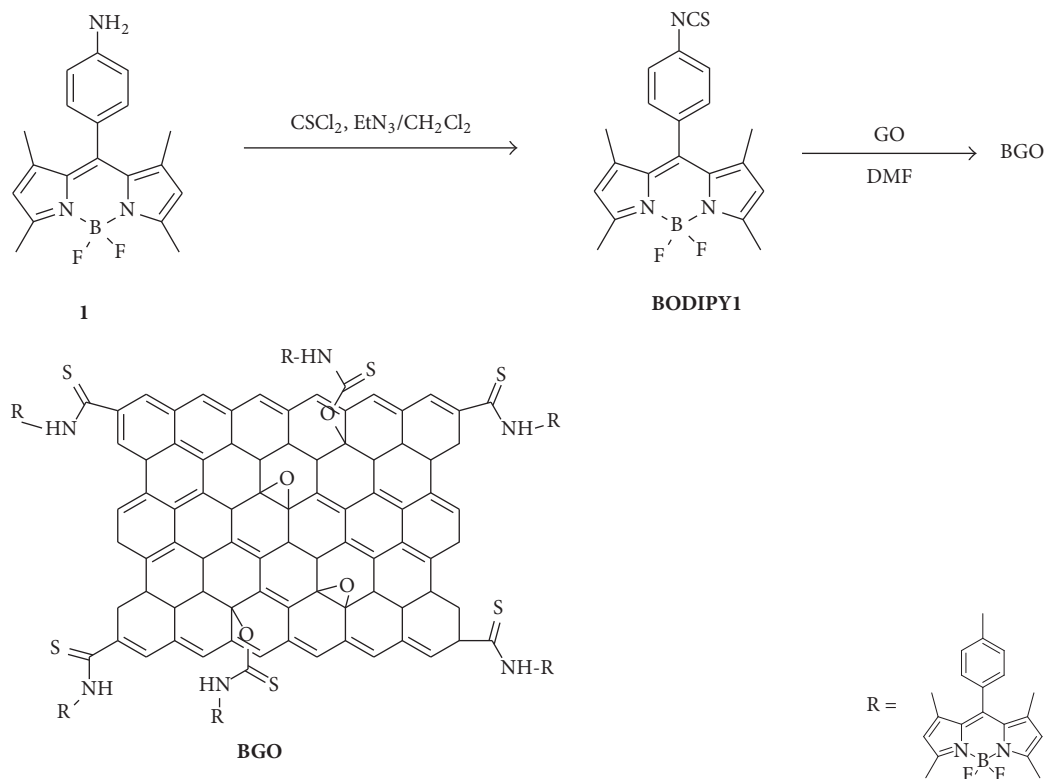
Scheme 1: Synthesis of **BGO**.

over anhydrous $MgSO_4$, and filtered, and the solvent was evaporated. The residue was then passed through a very short pad of silica gel and the resulting BODIPY isothiocyanate was used without further purification for the following reaction (60 mg, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36 (d, 2H, 8.4 Hz, phenyl), 7.29 (d, 2H, 8.4 Hz, phenyl), 6.00 (s, 2H, pyrrolyl), 2.55 (s, 6H, $-CH_3$), 1.40 (s, 6H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): 156.0, 142.8, 134.0, 132.3, 129.6, 126.5, 121.5, 14.7, 14.6 ppm.

The graphite oxide was prepared by oxidation of natural graphite powder (325 mesh) according to the method developed by Hummers Jr. and Offemann [14].

Preparation of BGO. Graphite oxide (20 mg) was dispersed in 10 mL DMF and sonicated for 3 hours. 40 mg **BODIPY 1** was added to the dispersion and the mixture was allowed to stir under nitrogen at 60°C for 24 h. Then the reaction mixture was poured into methylene chloride (30 mL) to coagulate the product. The product was filtered, washed with additional methylene chloride (100 mL), and dried under vacuum to afford **BGO**.

The ^{1}H and ^{13}C NMR spectra were collected on Jeol JNM-AL300 spectrometer at 300 MHz and 75 MHz, respectively. FT-IR experiments were conducted on a JASCO FT/IR-4200 spectrometer ($0.5 cm^{-1}$, 64). HRMS spectra were recorded on Jeol JMS-700 spectrometer. UV-vis absorption spectra were obtained on a Shimadzu UV-3100 spectrophotometer. Fluorescence spectra were recorded with a FL-4500 spectrofluorophotometer (EX 480 nm, Slit 5 nm). Atomic force microscopy (AFM) was taken on Bruker dimension icon.
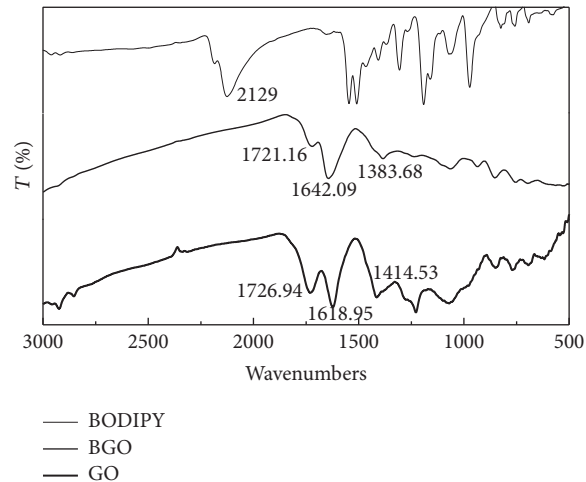
Figure 1: FT-IR spectra of GO, BGO, and **BODIPY 1**.

3. Results and Discussion

Figure 1 illustrates the changes occurring in the FT-IR spectra of **BODIPY 1**, GO, and **BGO**. The most characteristic features in the FT-IR spectrum of GO are the absorption bands corresponding to the C=O stretching at $1727 cm^{-1}$, the O-H deformation vibration at $1414 cm^{-1}$, the C-OH stretching at $1229 cm^{-1}$, and the C-O stretching at $1071 cm^{-1}$; besides the O-H stretches at $3400 cm^{-1}$ (not shown), the vibration of the absorbed water or skeletal vibrations of unoxidized

(a)

(b)
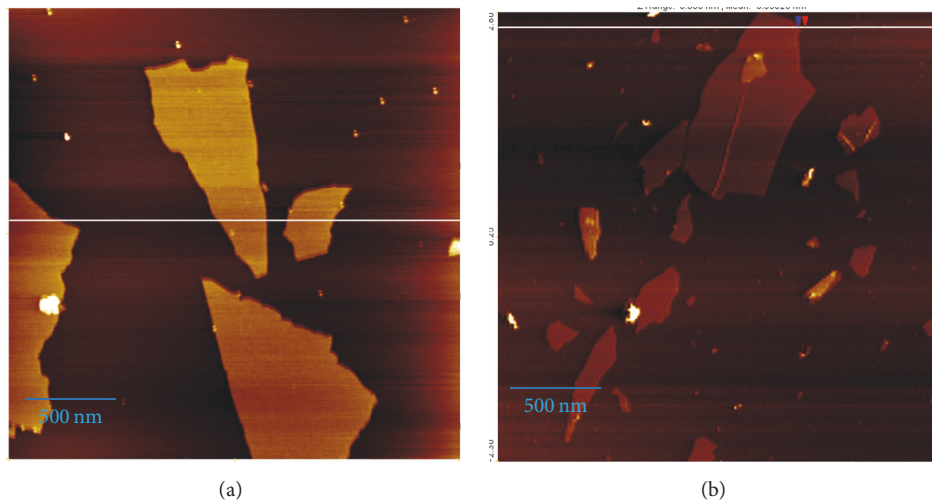
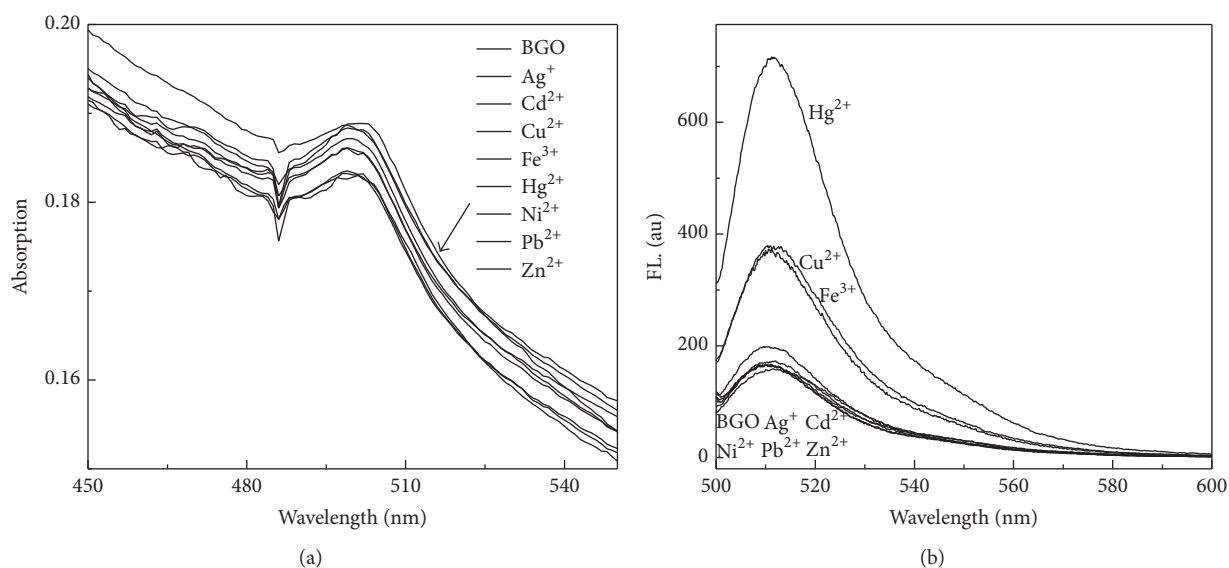Figure 2: The atomic force microscopy spectrum of (a) GO and (b) BGO.

(a)

(b)

Figure 3: (a) UV-vis spectra and (b) fluorescent spectra (excitation was at 480 nm) for BGO (0.02 mg/mL) in DMF without and with 400 μM metal ions.

graphitic domains at $1621\,cm^{-1}$ [11]. Upon treatment with **BODIPY 1**, the C=O stretching vibration at $1727\,cm^{-1}$ in GO becomes obscured by the appearance of a weaker absorption at $1721\,cm^{-1}$ that may be attributed to the consumption of carbonyl group. The new stretch at $1642\,cm^{-1}$ may be assigned to the thioamide stretching. And the adsorption bands corresponding to the NCS at $2183\,cm^{-1}$ and $2125\,cm^{-1}$ disappeared in **BGO** which indicated that the **BODIPY 1** was consumed during the reaction [11] and no free **BODIPY 1** was absorbed by GO.

AFM was performed to check the topology of GO and **BGO**. The GO and **BGO** samples (1 mg/mL in DMF, respectively) were prepared by spin-coating on a fresh mica surface. Figure 2 is the tapping mode AFM images of GO (a) and **BGO** (b). As shown in the AFM analysis, the average thickness for GO sheets was about 1.1 nm, and the average thickness

for **BGO** sheets was about 1.3 nm. This suggested that the **BGO** was single layer and the GO may be functionalized by **BODIPY 1**.

The effects of metal ion addition on the absorption and fluorescence properties of **BGO** in DMF were investigated to evaluate the metal ion binding properties of **BGO**. There is no change in absorption spectra upon addition of metal ions (Figure 3(a)). The fluorescence spectra of **BGO** (0.02 mg/mL) were recorded in following 480 nm excitation. Figure 3(b) showed the fluorescence spectra of compound **1** upon the addition of various kinds of metal ions, Ag^+, Cd^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}. After addition of Hg^{2+}, the emission at 510 nm was increased about 4-fold and almost no changes of **BGO** were observed in the presence of Ag^+, Cd^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} (400 μM), respectively. The free **BGO** solution exhibited fluorescence (excited at 480 nm) in DMF, but the
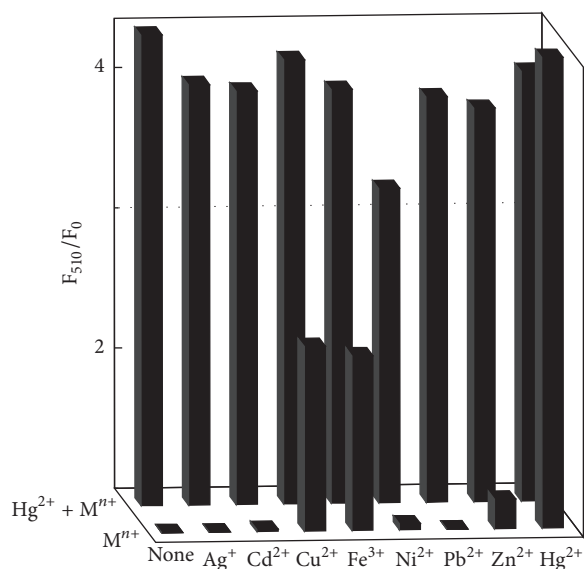
Figure 4: Fluorescence intensity change profiles of 0.02 mg/mL of BGO in DMF in the presence of selected metal ions (the concentration of Hg^{2+} and other metal ions was $400 \mu M$, respectively). The excitation wavelength was 480 nm, and the emission was monitored at 510 nm.

fluorescence of BGO was quenched dramatically compared to **BODIPY 1** (Figure S1 in the Supplementary Material available online at https://doi.org/10.1155/2017/9431605); the reason can be attributed to two possible competitive processes: photo-induced electron transfer (PET) and energy transfer (ET) [15]. The PET of **BODIPY 1** could not be inhibited after addition of Hg^{2+} because of desulfurization; the fluorescence of **BODIPY 1** would be quenched about 50% through the lone pair electrons on nitrogen (Figure S1b). However, the PET or ET would be suppressed by Hg^{2+} due to its strong thiophilic affinity of Hg^{2+}; therefore the fluorescence of **BGO** was increased. The result could be supported by FT-IR spectra. From the FT-IR spectra of **BGO** in presence of Hg^{2+}, the peaks correspond to C=O and thioamide would be red shift. That indicates the carbonyl group and thioamide participate in the binding with Hg^{2+} (Figure S2). Furthermore, the fluorescence of **BGO** in presence of Hg^{2+} would be reversed by addition of KI, which means that no desulfuration occurred (Figure S3).

To study the recognition of hybrid material for metal ions, the selectivity of **BGO** towards Ag^+, Cd^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Hg^{2+} was also examined at the concentration of $400 \mu M$ in DMF. As shown in Figure 4, the competition experiments revealed that the Hg^{2+}-induced luminescence enhancement was almost unaffected in the presence of Ag^+, Cd^{2+}, Cu^{2+} Ni^{2+}, Fe^{3+}, and Zn^{2+}; only Ni^{2+} showed a little interference, confirming the remarkable high selectivity of **BGO** for Hg^{2+}.

Titration experiments were performed with **BGO** (0.01 mg/mL) with different concentrations of Hg^{2+} ranging from 0 to $125 \mu M$ in 2 ml DMF. Figure 5 illustrated the fluorescence titration spectra of **BGO** upon addition of
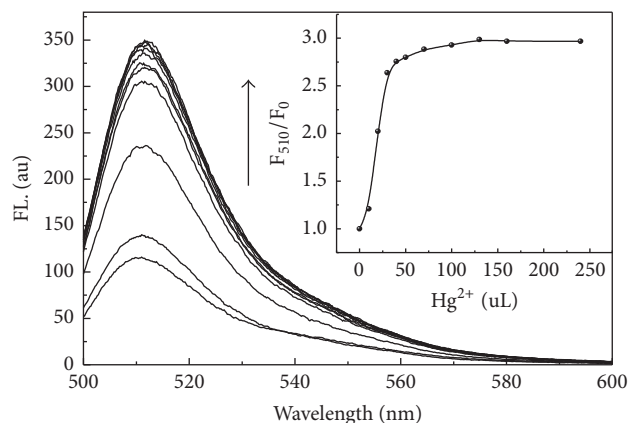

Figure 5: Fluorescence spectra of **BGO** (0.01 mg/mL) complex with different concentrations of Hg^{2+} ranging from 0 to $125 \mu M$ in 2 ml DMF.

various amounts of Hg^{2+} (0, 5, 10, 15, 20, 25, 35, 50, 60, 80, and $125 \mu M$). As shown in Figure 5, the fluorescence intensity increased continuously with increasing Hg^{2+} concentration. The inset showed the fluorescence titration profile of **BGO** at 510 nm upon addition of Hg^{2+}.

4. Conclusions

In conclusion, an organic-inorganic hybrid complex **BGO** has been synthesized. And the **BGO** can be used as a selective fluorescent sensor for Hg^{2+}. Further studies on the accurate structure of the **BGO**-Hg^{2+} complex and other application of **BGO** are in progress in our laboratory. In addition, the present work inspires the development of multifunctional GO-based hybrid materials through a simple charge-transfer process. Taking advantage of the high surface area of GO, the organic-inorganic hybrid complex based on GO could be potentially used for treating wastewater and sustained drug release.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
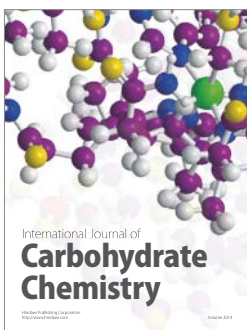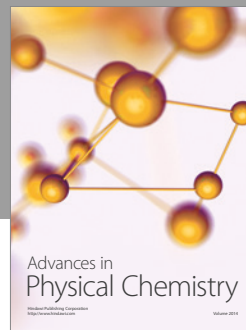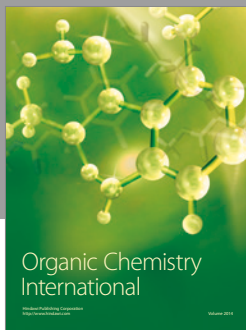
Acknowledgments

References

[1] , *Fluorescent Chemosensors for Ion and Molecule Recognition*, A. W. Czarnik, Ed., American Chemical Society, Wash, USA, 1993.

[2] E. Merian, "Metals and Their Compounds in the Environment," in *Metals and Their Compounds in the Environment*, Merian, E.,

VCH: Weinheim, R. von Burg and M. R. Greenwood, Eds., pp. 1045–1088, VCH, Weinheim, Germany, 1991.

[3] Y. D. Fernandez, A. P. Gramatges, V. Amendola et al., "Using micelles for a new approach to fluorescent sensors for metal cations," *Chemical Communications*, vol. 10, no. 14, pp. 1650-1651, 2004.

[4] L.-L. Wu, Z. Wang, S.-N. Zhao et al., "A Metal-Organic Framework/DNA Hybrid System as a Novel Fluorescent Biosensor for Mercury(II) Ion Detection," *Chemistry - A European Journal*, vol. 22, no. 2, pp. 477–480, 2016.

[5] P. Zhou, Q. Meng, G. He, H. Wu, C. Duan, and X. Quan, "Highly sensitive fluorescence probe based on functional SBA-15 for selective detection of Hg2+ in aqueous media," *Journal of Environmental Monitoring*, vol. 11, no. 3, pp. 648–653, 2009.

[6] W. S. Han, H. Y. Lee, S. H. Jung, S. J. Lee, and J. H. Jung, "Silica-based chromogenic and fluorogenic hybrid chemosensor materials," *Chemical Society Reviews*, vol. 38, no. 7, pp. 1904–1915, 2009.

[7] O. C. Compton, D. A. Dikin, K. W. Putz, L. C. Brinson, and S. T. Nguyen, "Electrically conductive "alkylated" graphene paper via chemical reduction of amine-functionalized graphene oxide paper," *Advanced Materials*, vol. 22, no. 8, pp. 892–896, 2010.

[8] S. T. Huang, Y. Shi, N. B. Li, and H. Q. Luo, "Fast and sensitive dye-sensor based on fluorescein/reduced graphene oxide complex," *Analyst*, vol. 137, no. 11, pp. 2593–2599, 2012.

[9] M. Kollmannsberger, K. Rurack, U. Resch-Genger, and J. Daub, "Ultrafast charge transfer in amino-substituted boron dipyrromethene dyes and its inhibition by cation complexation: A new design concept for highly sensitive fluorescent probes," *The Journal of Physical Chemistry A*, vol. 102, no. 50, pp. 10211–10220, 1998.

[10] M. Yuan, Y. Li, J. Li et al., "A colorimetric and fluorometric dual-modal assay for mercury ion by a molecule," *Organic Letters*, vol. 9, no. 12, pp. 2313–2316, 2007.

[11] S. Stankovich, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, "Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets," *Carbon*, vol. 44, pp. 3342–3347, 2006.

[12] R. Ziessel, L. Bonardi, P. Retailleau, and G. Ulrich, "Isocyanate-, isothiocyanate-, urea-, and thiourea-substituted boron dipyrromethene dyes as fluorescent probes," *The Journal of Organic Chemistry*, vol. 71, no. 8, pp. 3093–3102, 2006.

[13] M. Li, H. Wang, X. Zhang, and H.-S. Zhang, "Development of a new fluorescent probe: 1,3,5,7-tetramethyl-8-(4′-amino-phenyl)-4,4-difluoro-4-bora-3a, 4a-diaza-s-indacence for the determination of trace nitrite," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 60, no. 4, pp. 987–993, 2004.

[14] W. S. Hummers Jr. and R. E. Offeman, "Preparation of graphitic oxide," *Journal of the American Chemical Society*, vol. 80, no. 6, p. 1339, 1958.

[15] Y. Xu, Z. Liu, X. Zhang et al., "A graphene hybrid material covalently functionalized with porphyrin: synthesis and optical limiting property," *Advanced Materials*, vol. 21, no. 12, pp. 1275–1279, 2009.