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# Synthesis of A<sub>3</sub>B zinc tetrapyrazinoporphyrazine covalently functionalized reduced graphene oxide

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ABSTRACT

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In this paper, novel strategy was applied to the preparation of tetrapyrazinoporphyrazine-reduced graphene oxide hybrid material. Reduced graphene oxide was functionalized with carboxylic acid groups via diazotization with 4-aminio benzoic acid and subsequent amidation with the synthesized aminoalkyl-tetrapyrazinoporphyrazine. FT-IR, Raman, TGA, UV-vis and fluorescence spectrophotometry methods were utilized for characterization of the hybrid material, which exhibited an electron/energy transfer ability.

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1

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#### Tetrahedron

Graphene, a flat carbon surface composed of sp<sup>2</sup> carbon atoms in a honeycomb structure, has attracted much research attention due to its remarkable electrical, thermal and mechanical properties, which have facilitated a variety of applications.<sup>1, 2</sup>

To enhance the processibility and performance of graphene material, the introduction of functional groups to the graphene sheet as graphene oxide (GO) or inorganic/organic functionalized graphene has been investigated. Recently, photoactive components such as phthalocyanines, porphyrins, and diketopyrrolopyrroles were covalently attached to graphene, yielding unique optoelectronic properties.<sup>3-5</sup>

The attachment of phthalocyanine to graphene has been explored through many strategies such as physical bonding and covalent bonding with GO, reduced GO (rGO) or chemically functionalized graphene.<sup>6-9</sup> For covalent bonding between phthalocyanine and graphene, the most common method is an esterification reaction with GO and subsequent *in-situ* reduction. To obtain milder reaction conditions, another method in which a functional group was introduced for attachment of the phthalocyanine through a 1,3-dipolar cycloaddition or diazonium reaction was developed.<sup>10</sup> As-prepared phthalocyanine-graphene hybrid materials have been investigated in various uses including photocatalyst, capacitor, optical limiting materials, oxygen reduction reaction, and sensors.<sup>6, 8, 11-14</sup>

Tetrapyrazinoporphyrazines, the aza-analogues of phthalocyanines in which the benzene rings are replaced with pyrazines, were discovered in the early 1960s. Interest in their synthesis and photophysical properties has increased during the last decade because of their strong absorption and emission in the red to near-IR region, which is desirable for photochemical applications.<sup>15-17</sup>

Moreover, 2,3-dicyanopyrazines, the precursors of azaphthalocyanine, are comparatively easy to prepare, and their numerous derivatives have been designed and prepared for potential use biologically active materials.<sup>18</sup> The classical synthesis of 2,3-dicyanopyrazines involves the condensation of diaminomaleonitrile (DAMN) with 1,2-dicarbonyl compounds. This facile reaction is the most widely used synthetic method for preparing 2,3-dicyanopyrazine derivatives.<sup>19</sup>

In the present paper, novel strategy was developed for the preparation of a tetrapyrazinoporphyrazine-graphene hybrid material. A zinc tetrapyrazinoporphyrazine derivative bearing 1° amine groups was synthesized in  $A_3B$  form and graphene was modified through oxidation, reduction, and direct diazotization of the sp<sup>2</sup> carbon network using 4-amino benzoic acid.<sup>20</sup> Finally, an amide linkage was formed between the synthesized zinc tetrapyrazinoporphyrazine covalently functionalized with rGO. The hybrid material was characterized with UV-vis spectrophotometer, fluorescence spectrophotometry, Fourier transform infrared (FT-IR) and Raman spectroscopy, and thermogravimetric analysis (TGA).

The synthetic routes used to prepare the functionalized precursors and the hybrid material are presented in scheme 1 and scheme 2, respectively. The starting materials, 1-(6-bromohexyl)-1H-pyrrole-2,5-dione, 1,2-bis{4-(*tert*-butyl)phenyl}ethane-1,2dione (2a) and 1,2-bis(4-hydroxyphenyl)ethane-1,2-dione were prepared using a reported method.<sup>21-23</sup> 2a and 2b, which were prepared through substitution reaction, underwent condensation with DAMN, resulting in production of the precursors of azaphthalocyanine. As-prepared pyrazines, 3 were used to prepare magnesium tetrapyrazinoporphyrazine. After demetallization, the metal-free A<sub>3</sub>B azaphthalocyanine was separated using column chromatography on silica gel and subsequently reacted with zinc acetate, yielding 4. Finally, the target compound 5 was prepared through phthalimide deprotection. For the graphene precursors, GO, prepared using Hummers method,<sup>20</sup> and was reduced using 50% hydrazine monohydrate. For introduction of carboxylic acid groups, 4-



**Scheme 1**. Synthetic route of tetrapyrazinoporphyrazine: (i) **3a**: *p*-TsOH, EtOH, 86%; **3b**: AcOH, reflux, 80%; (ii) Mg, I<sub>2</sub>, *n*-butanol, reflux; *p*-TsOH, THF, r.t., 17%; (iii) Zn(OAc)<sub>2</sub>, pyridine, reflux, 78%; (iv) hydrazine monohydrate, THF, EtOH, r.t., 81%.

2

amino benzoic acid and isopentyl nitrite were added to a suspension of exfoliated rGO in water.<sup>20</sup> Finally, the functionalized rGO was produced through condensation with the amine group of **5** in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) and 4-dimethyl-aminopyridine (4-DMAP) as catalyst in DMF solvent, leading to formation of amide groups.<sup>12</sup> Details of the experimental procedures are described in Supplementary Data.

Figure S1 and S2 show UV-vis spectra and fluorescence spectra of **4** and **5** in common organic solvents, respectively, and the numerical results are summarized in Table 1. **4** primarily displays a monomeric absorption band in THF but exhibits aggregation behavior in other solvents. **5** is soluble in polar solvent such as methanol, DMF, and DMSO, with little aggregation behavior observed in DMSO. On the other hands, the fluorescence quantum yield of **5** was much lower than that of **4**, which is ascribed to the nonbonding electron pair of the amino nitrogen transferring to the excited fluorochrome, leading to fluorescence quenching.<sup>24</sup> We confirmed that the amine group could act as a fluorescence quencher in photo-induced electron transfer process (PET) through an additional experiment, carried out through the addition of trifluoroacetic acid. (Figure S3)

Table 1. Photophysical and photochemical data for compound **4** and **5**.

Comp.	$\lambda_{max}$	$\lambda_{em}^{c}$	log e	$\Phi_{\rm F}^{\rm d}$
p ·	B / Q band	cili	8 -	- 1
4	375 / 650 <sup>a</sup>	660 <sup>a</sup>	5.00	$0.06^{a} / 0.15^{b}$
5	384 / 661°	668°	4.97	0.05 "
	<u></u>			соон
ноос		ЮН		
CE				
For the second s		<u> </u>	+ F	II.
Č	COOH OH	ОН	Z	TT
	<i>t</i> -E	Bu	<i>t</i> -Bu	6
		$\langle \rangle$	$\langle \rangle$	
		NŰ	Ň	
t-	Bu		LN	<i>t</i> -Bu
ii			N	
		, N Zr		
t-	Bu	N⊰N	≻N	t-Bu
		N	N	. 24
			<u> </u>	
		$\langle \rangle$		
		0	0~	_
0	HN-//			NH2
6				
L		7		
	-			
E	TT			
Zer	1D			

**Scheme 2**. Functionalization of rGO: (i) 50% hydrazine, H<sub>2</sub>O, reflux; 4-aminobenzoic acid, isopentyl nitrite, 80 °C; (ii) **5**, EDCI, 4-DMAP, DMF, 90 °C.

a) in THF, b) in DMSO, c) excited at 590 nm, d) determined by comparison  $\Phi_F$  with unsubstituted zinc phthalocyanine ( $\Phi_F = 0.32$ , in THF).

The IR spectrum of GO has absorption bands corresponding to C=O carbonyl stretching at 1733 cm<sup>-1</sup>, O-H stretching around 3300 cm<sup>-1</sup>, O-H deformation vibration at 1412 cm<sup>-1</sup>, C-OH stretching at 1226 cm<sup>-1</sup>, and C-O stretching at 1050 cm<sup>-1</sup>, as shown in Figure 1. The reduction of GO significantly decreased oxygen functional groups after the deoxygenation reaction.<sup>25</sup> After diazotization with 4-aminobenzoic acid, the characteristic absorption bands of **6** showed O-H stretching above 3000 cm<sup>-1</sup> and a C=O carbonyl stretching band at 1684 cm<sup>-1</sup>. As expected, the IR spectrum of **7** showed a characteristic amide stretching vibration peak at 1655 cm<sup>-1</sup> and a finger-print region similar to that of **5**.

The significant structural changes in the conversion of GO to 7 are reflected in their Raman spectra. (Figure 2) The Raman spectrum of GO displays prominent bands at 1343 cm<sup>-1</sup> and 1589  $cm^{-1}$  with an I<sub>d</sub>/I<sub>g</sub> of 0.94. In the Raman spectrum of rGO, the G band was shifted to 1340 cm<sup>-1</sup>, with a D/G intensity of 1.24. This increase in D/G intensity ratio compared with that of GO, indicate a decrease in the average size of the sp<sup>2</sup> domain upon reduction of GO.<sup>26</sup> After introduction of carboxylic acid to the rGO, the Raman spectrum of 6 contained G and D bands at 1340 cm<sup>-1</sup> and 1584 cm<sup>-1</sup>, respectively, and a decreased D/G intensity ratio (1.19) compared to that of rGO. This result is not in accordance with previous reports. The D band has been used to monitor the process of covalent functionalization which transform  $sp^2$  to  $sp^3$  sites, whereas the G band can be used to estimate the level and distribution of modifications. For this reason, the  $I_d/I_g$  ratio would be enhanced after functionalization of rGO.<sup>27</sup> In the present study, although some sp<sup>2</sup> carbon atoms in rGO were transformed to sp<sup>3</sup> carbon atoms, they were present in a smaller amount than in 6. In this same vein, the D/G intensity ratio decreased from 1.19 for 6 to 1.17 for 7.

Figure 3 shows absorption band of **5**, **6**, and **7** in DMSO. **7** has two broad band at 383 nm and 659 nm, resulting from the B and Q bands of **5**, respectively. This results provides support that **5** was attached to rGO.

### Tetrahedron







spectra of 5 and 7.

TGA curves of the compounds are shown in Figure 4. GO is thermally unstable and experiences a major loss at temperatures higher than 200 °C due to pyrolysis of labile oxygen-containing functional groups.<sup>26</sup> In contrast to GO, rGO shows much improved thermal stability. Only 11.8% weight loss was observed at 800 °C due to decomposition of residual oxygencontaining functional groups. In the case of 6, weight loss occurred around 300 °C, and approximately 33% weight loss was observed at 800 °C, which is ascribed to decomposition of introduced benzoic acid groups in the material. In the TGA curve of tetrapyrazinoporphyrazine 5, subsequent decomposition was observed, below 300 °C, a slight mass loss occurred, while significant mass loss was observed between 400 °C and 550 °C. On the other hands, hybrid material 7 exhibited gradual decomposition and higher thermal stability than 6. At 800 °C, the amount of residual 7 was 73.8%, whereas the amount of residual **6** was 66.7%.

In summary, zinc tetrapyrazinoporphyrazine bearing amine groups was synthesized for attachment to graphene and novel



Figure 4. TGA profiles of GO, rGO, 5, 6, and 7, measured under nitrogen. (heating rate : 5 °C / min)

Fluorescence spectra of **5** and **7** were created in DMSO with excitation at 590 nm. Before measurement of emission, the concentration of **5** and **7** were chosen to provide a 0.22 absorption intensity at the excitation wavelength. After attachment to rGO, the maximum fluorescence peak of **7** was blue-shifted by 16 nm and the intensity was apparently decreased by 91%, indicating that intramolecular energy or charge transfer occurred from the tetrapyrazinoporphyrazine to rGO.<sup>28, 29</sup>

functionalization of rGO through diazotization and subsequent amidation was successfully employed to prepare tetrapyrazinoporphyrazine covalently functionalized reduce graphene oxide. The synthesized compounds were characterized using <sup>1</sup>H-NMR and MALDI-TOF mass spectroscopy. FT-IR, Raman, TGA and UV-vis spectrophotometry methods supported the formation of the intermediates and final product in this approach for preparing graphene hybrid material. The quenched fluorescence of the hybrid material exhibited energy or electron transfer ability from tetrapyrazinoporphyrazine to rGO. It is

4

expected that this hybrid material will be applied to optoelectric devices.

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#### Supplementary data

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5

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