# **Electronic Supplementary Information**

Covalent Functionalization of Graphene Oxide with Porphyrin and

Porphyrin Incorporated Polymers for Optical Limiting

Yinlong Du,<sup>a</sup> Ningning Dong,<sup>b</sup> Menghan Zhang,<sup>a</sup> Kai Zhu,<sup>a</sup> Ruiqi Na,<sup>a</sup> Shuling Zhang,<sup>a</sup> Ningwei Sun,<sup>a</sup> Guibin Wang<sup>a\*</sup> Jun Wang,<sup>b\*</sup>

<sup>[a]</sup> College of Chemistry, The Alan. G. Macdiarmid laboratory, Jilin University, Changchun 130012, (P. R. China)
\*Prof. Guibin Wang Tel: (+86) 0431 85168889. Fax: (+86) 0431 85168889.
E-mail: wgb@jlu.edu.cn
<sup>[b]</sup> Key Laboratory of Materials for High-Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201900, (P. R. China)

E-mail: jwang@siom.ac.cn

## **Experimental Section**

#### Materials

GO was prepared using the Hummers method from graphite powder.<sup>1</sup> (*p*-amino)phenylhydroquinone (APH) was synthesized according to the literature.<sup>2</sup> Bis(4-fluorophenyl) sulfone (99%) was provided by TCI Shanghai development Co. Ltd., China. Anhydrous THF was distilled from sodium, *N*,*N*-dimethylformamide (DMF) and trimethylamine were dried and distilled from CaH<sub>2</sub> prior to use. Other chemicals and reagents were used as received without further purification.

## Synthesis of ZnTNP-PAES

5,15-*bis*(4-hydroxyphenyl)-10,20-dinaphthylporphyrin (*trans*-DHTNP) was synthesized by Alder's method.<sup>3</sup> the crude product was purified by chromatography (CHCl<sub>3</sub>: methane, 50: 1). The third fraction was collected and evaporated to give bright purple crystalline 5,15-*bis*(4-hydroxyphenyl)-10,20-dinaphthylporphyrin (yield: 5.6%). Anal. Calcd for (C<sub>52</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>): C 83.63, H 4.59, N 7.50. Found: C 83.21, H 4.70, N, 7.22%. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, TMS),  $\delta$  (ppm): 9.96 (s, 2H, OH), 8.9 (s, 2H, pyrrolic- $\beta$ -CH). 8.79-8.82 (d, 2H, pyrrolic- $\beta$ -CH), 8.51-8.54 (m, 2H, naphthyl CH), 8.46-8.50 (m, 4H, pyrrolic- $\beta$ -CH), 8.20-8.32 (m, 4H, naphthyl CH), 8.01-8.03 (d, 4H, J = 7.1 Hz, *ortho*-C<sub>6</sub>H<sub>4</sub>OH), 7.48-7.53, 7.88-7.94 (m, 4H, naphthyl CH), 7.18-7.21 (d, 4H, J = 8.7 Hz, *meta*-C<sub>6</sub>H<sub>4</sub>OH), 6.92-7.15 (m, 4H, naphthyl CH), -2.58 (s, 2H, NH). MALDI-TOF MS: calculated for (C<sub>52</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>): m/z [M + H]<sup>+</sup> = 747.27; found: m/z = 748.5.

The synthetic procedure of ZnTNP-PAES was illustrated in **Fig. S1** according to previous literature,<sup>4</sup> *trans*-DHTNP 2.239 g, APH 1.407 g, *bis*(4-fluorophenyl) sulfone 2.540 g, and anhydrous  $K_2CO_3$  1.52 g, were dissolved in 21 mL tetramethylene sulfone and 12 mL toluene with mechanical stirring in a nitrogen atmosphere. The mixture was refluxed at 130 °C to remove the resulting water through a Dean-stark trap, then heated to 180 °C for 6 h to complete the polymerization. The viscos solution was poured into deionized water to precipitate the thread-like dark purple polymer. After being pulverized into powders, the polymer was washed with boiled water and ethanol to remove the solvent and monomer residues, the product was dried at 100 °C for 24 h to give TNP-PAES.

Using a similar method according to previous literature, the precursor polymer (2.0 g) was dissolved in *N*,*N*-dimethylacetamide (DMAc) and stirred with excess  $Zn(OAc)_2 \cdot 2H_2O$  at 80 °C for 4 h. The polymer solution was precipitated into deionized water, washed with water to remove the excess acetate, and then isolated by filtration before being dried to give the final product ZnTNP-PAES (purple solid). Yield: 90%,  $M_n$ : 26.2 kg mol<sup>-1</sup>,  $M_w$ : 61.7 kg mol<sup>-1</sup>, PDI: 2.35,  $T_g$  (DSC): 260.1 °C.

## Synthesis of ZnTNP-PAES functionalized hybrid PF-GO and PF-RGO

100 mg GO was dispersed in a large excess of thionyl chloride (60 mL) containing a catalytic amount of DMF under sonication for 3 h, and stirred at 60 °C for 24 h under purified argon. After the removal of thionyl chloride under reduced pressure, the solid was washed with anhydrous THF and filtered. To the suspension of activated GO-COC1 in anhydrous DMF (50 mL) was added ZnTNP-PAES (400 mg) and trimethylamine (5 mL), the reaction was stirred at 80 °C for 72 h under purified argon, after which the functionalized GO were isolated by washing off the unreacted ZnTNP-PAES with excess DMF, filtered through a single layer nylon membrane (0.22  $\mu$ m) several times until no absorption (*Soret* band) in UV-vis spectrum could be detected in the filtrate. The generated trimethylamine salts was removed by dispersing the PF-GO hybrid in water. Finally the hybrid was collected by filtration, and dried in vacuum at 50 °C for 24 h to give dark brown product.

The reduced GO hybrid PF-RGO was prepared by adding hydrazine monohydrate (3 mL, 85 wt% in water) to a PF-GO aqueous dispersion (500 mL, 0.1 mg mL<sup>-1</sup>). After vigorous stirring, the mixture was kept at 80 °C for 24 h, then filtered and washed with water and methanol thoroughly, and dried in vacuum at 80 °C to obtain the PF-RGO sample as black powder.

## Synthesis of ZnTNP functionalized hybrid ZnP-GO and ZnP-RGO

500 mg 5-(4-hydroxyphenyl)-10,15,20-trinaphthylporphyrin zinc (ZnTNP-OH) was prepared according to previous report.<sup>5</sup> GO (100 mg) was treated with thionyl chloride using the same method above. ZnTNP-OH and 5 mL trimethylamine were added to 50 mL anhydrous DMF suspension of GO-COCl. The reaction was continued at 80 °C for 72 h under the protection of pure argon. After cooling to room temperature, the

suspension was filtered through a single layer nylon membrane and washed extensively with DMF. Sonication and redispersion were repeated in chloroform to remove the absorbed porphyrins, then the hybrid was dispersed in water to remove the trimethylamine salts. The final product was collected by filtration and dried at 50 °C for 24 h to give ZnP-GO hybrids as brown solid.

The reduced hybrid ZnP-RGO was prepared using a similar procedure as that of PF-RGO. Hydrazine monohydrate (3 mL, 85 wt% in water) was added to a ZnP-GO aqueous dispersion (500 mL, 0.1 mg mL<sup>-1</sup>) with vigorous stirring, the reaction was kept at 80 °C for 24 h, then the product was filtered and washed with water and methanol thoroughly, and dried in vacuum to obtain ZnP-RGO as black powder.

#### Characterization

IR spectra were recorded on a Nicolet Impact 410 Fourier transform infrared spectrophotometer in transmittance. Thermogravimetric analysis (TGA) was recorded on a Netzch Sta 449 thermal analyser system in nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Raman spectra were obtained on a LabRAM HR Evolution (Horiba) Raman microscope, excited at 532 nm with Arion laser radiation. Wide-angle X-ray diffraction were performed on a Rigaku D/max-2500 X-ray diffractometer with CuKa radiation ( $\lambda = 0.154$  nm) as the X-ray source. Scanning electron microscopic (SEM) images were obtained on a FEI Nova NanoSEM 450 microscope. Transmission electron microscopic (TEM) images were taken on a JEM-1200EX electron microscopic operated at an acceleration voltage of 100 kV, dilute dispersion of the GO hybrid samples in water were dropped onto the copper grids and dried for TEM image. X-ray photoelectron spectra was measured on PHI-1600 X-ray photoelectron spectrometer using Mg Ka (1253.6 eV) radiation as the radiation source. UV-vis absorption spectra was performed on UV2501-PC spectrophotometer. Fluorescence spectra and fluorescence lifetime measurement were recorded on a FLS 920 steady-transient spectrophotometer with a time-correlated single-photon counting system using 400 nm laser source.

The nonlinear optical measurements were performed using an open aperture Z-scan technique employing a Q-switched Nd:YAG laser of 6 ns pulses at 532 nm and 1064 nm with a repetition of 10 Hz. As shown in **Fig. S5**, the laser beam was focused with a 15 cm focus lens, and all samples were placed in a 5 mm  $\times$  10 mm quartz cell and moved along the *z* direction. Two high-precision photo-detectors were used to monitor the reference and transmitted pulse energy. Meanwhile, another focusing lens at 45° to the incident beam was setup to collect the scattering signal. All samples were adjusted to have a linear transmittance of 65% at 532 nm in DMF. The optical arrangement is identical to the literature.<sup>6</sup>



**Fig. S1**. Synthesis of ZnTNP-PAES, and <sup>1</sup>H NMR spectrum of (a) porphyrin monomer *trans*-DHTNP and (b) ZnTNP-PAES.



Fig. S2. FTIR spectra of GO, ZnP-GO, ZnP-RGO and OH-ZnTNP.



**Fig. S3**. High-resolution C 1s XPS spectra of GO (a), PF-GO (b), and PF-RGO (c), N 1s XPS spectra of ZnTNP-PAES (d) and PF-GO (e).



Fig. S4. TEM (left) and SEM (right) images of GO sheets



**Fig. S5**. Transient fluorescence spectra of ZnTNP-PAES, PF-GO, and PF-RGO (a), OH-ZnTNP, ZnP-GO and ZnP-RGO (b).



Fig. S6. The typical experimental setup for Z-scan measurement.



**Fig. S7**. UV-vis absorption spectra of PF-GO-H and PF-GO-L with the same absorption profile of GO, and open-aperture Z-scan curves of PF-GO-H and PF-GO-L at 532 nm (left) and 1064 nm (right),



Fig. S8. Open-aperture Z-scan curves and  $\beta_{\text{eff}}$  values of PF-GO in DMF at 532 nm for different pulse energy.



Fig. S9. Open-aperture Z-scan curves and  $\beta_{\text{eff}}$  values of PF-GO in DMF at 1064 nm for different pulse energy.

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