### Supporting Information- PY-COM-08-2019-001284

## **Donor-Acceptor Type Black Phosphorus Nanosheets Covalently Functionalized** with Conjugated Polymer for Laser Protection

Kexin Wang,<sup>a</sup> Ningning Dong,<sup>b,c</sup> Zhiwei Liu,<sup>a</sup> Bin Zhang,<sup>a</sup> Jun Wang,<sup>\*b,c</sup> Yu Chen<sup>\*a</sup>

<sup>a</sup>Key Laboratory for Advanced Materials, Institute of Applied Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China. Email: chentangyu@yahoo.com

<sup>b</sup>Laboratory of Micro-Nano Optoelectronic Materials and Devices, Key Laboratory of Materials for High-Power Laser, Shanghai Institute of Optics and Fine Mechanics,

CAS, Shanghai 201800, China. Email: jwang@siom.ac.cn

<sup>c</sup>State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China

# **Experimental section**

## 1. Materials

Reagents for preparation were purchased from Aladdin. Unless statement otherwise, all the chemicals were used without further treatment. All organic solvents were redistilled under dry nitrogen. All the operations were performed under purified nitrogen. The black phosphorus (BP) crystals (99.98%) were purchased from Xian Feng Nano Company (China) and kept in a glove box filled with Ar before use. 1,4-diethynyl-2,5-bis(hexyloxy)benzene was synthesized according to the literatures.<sup>1,2</sup>



Scheme 1. Synthesis of 1,4-diethynyl-2,5-bis(hexyloxy)benzene

Preparation of few-layer BP

By using liquid exfoliation technique that has been widely used to exfoliate various layered-materials producing single- and/or few-layer nanosheets, we prepared few-layer BP nanosheets with very regular and uniform structural feature. In a typical procedure, 50 mg of BP powder, which was obtained by grinding the BP crystals in the glove box, was added to 100 mL of anhydrous NMP, and then was sonicated for 5 hours in a water bath of 10-15<sup>o</sup>C until a homogeneous suspension was formed. After being centrifuged at 5000 rpm for 120 minutes, the superstratum dispersions were collected and kept in a dark bottle in nitrogen atmosphere. Before use, the above dispersions were centrifuged at high speed of 12000 rpm for 20 minutes. The collected solid few layer BP was directly used for the synthesis of 4-BBD-BP.

#### Synthesis of 4-BBD-BP

Few-layer BP was functionalized with the *p*-bromophenyl group through a spontaneous reaction between an aryl diazonium salt and BP under aqueous conditions to give bromo-functionalized BP (4-BBD-BP), which shows very good dispersibility in common organic solvents. In a typical reaction, a mixture of 4-bromobenzenediazonium tetrafluoroborate (81.24mg, 0.3mmol) and tetrabutylammonium hexafluorophosphate (1162 mg, 0.3 mmol) in acetonitrile (30 mL) was added dropwise to the stirred BP (30 mg) dispersion in acetonitrile, followed by vigorously stirring for 3h. After removal of solvent, the collected solid sample was physically agitated in a large volume of neat acetonitrile, and then washed with large amount of deionized water, and dried under vacuum for 6 h to give 4-BBD-BP.

## Synthesis of poly[(1,4-diethynyl-2,5-bis(hexyloxy)benzene)-*alt*-benzo[c]thiadiazole] (PDBT) covalently functionalized BP nanosheets (PDBT-BP)

4-BBD-BP (50 mg) was dispersed into anhydrous acetonitrile (50 ml). Then, this suspension was sonicated for 30 min before adding a mixture of 1,4-diethynyl-2,5-bis(hexyloxy)benzene(100 mg, 0.31mmol), 4,7-dibromobenzo[c] [1,2,5]thiadiazole (116 mg, 0.40 mmol), Pd[(PPh<sub>3</sub>)<sub>4</sub>](7 mg, 0.006 mmol), CuI(3 mg, 0.013 mmol), and Et<sub>3</sub>N (4 mL). After adding all the reactants, the mixture was heated

to 80 °C and stirred continuously for 72 h under  $N_2$  atmosphere. After completion of reaction, the crude product was vacuum-filtered through a polycarbonate film ( $\phi$ 0.22  $\mu$ m). The collected solid product was washed with methanol, acetone and deionized water until the filtrate was clear and transparent. After removing any possible unreacted monomer and soluble pure polymer (if any) trapped in the resultant product, the obtained solid was thoroughly vacuum-dried at 60 °C for 24 h to give 153 mg of brown-red powder.

**Preparation of PMMA-based films:** The sample (BP, PDBT, PDBT-BP, annealed PDBT-BT) in NMP was added to a cyclohexanone solution of PMMA (100 g.L<sup>-1</sup>) at a partial concentration  $\sim 2$  g.L<sup>-1</sup>. This was followed by sonic agitation until a well-dispersed solution was formed. By using multilayer conventional spin casting technique,<sup>3</sup> we achieved PMMA-based films which were further dried at 60°C for 24 h under high vacuum to remove any possible residual organic solvent before NLO measurements.

### 2. Measurements and Instruments

The ultraviolet-visible (UV/Vis) absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Fourier transform infrared (FTIR) spectra were performed on a Nicolet Nagma-IR 550 spectrophotometer using KBr pellets. Raman spectra were recorded on an Invia/Reflrx Laser Micro-Raman spectrometer (Renishaw, England) with excitation laser beam wavelength of 785 nm. Transmission electron microscopy (TEM) images were recorded on a JEOL-2100 (JEOL Ltd., Japan) TEM system operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250Xi (Thermo Fisher) with Al Ka radiation as X-ray source for radiation. Atomic force microscopy (AFM) measurement was performed on a Solver P47-PRO (NT-MDT Co., Moscow, Russia) microscope. The sample for the fluorescence measurement was dissolved in dry solvent, filtered, transferred to a long quartz cell, and then capped and bubbled with dry nitrogen for 15 min. A HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer

was used to record the steady-state fluorescence spectra. Thermogravimetric analysis (TGA) was carried out using TA instruments TGA-Q500.

The NLO and OL performances of the materials were investigated through a standard open-aperture Z-scan apparatus with 6 ns pulses from a Q-switched Nd:YAG laser at 532 nm. The laser beam was focused with a 15 cm lens. The repetition rete was set to 2 Hz. To evaluate their NLO responses, both the dispersions and films were adjusted to have similar linear transmittances of  $\sim$ 57% at 532 nm.

### 3. Figures



Figure S1. FTIR spectra of the samples.



Figure S2: AFM image of the PDBT-BP/PMMA film.



Figure S3. TGA thermogram of PDBT-BP measured in N<sub>2</sub>.

## References

- 1. B. Liu, Y. Bao, F. Du, H. Wang, J. Tian, R. Bai, *Chem. Commun.* 2011, 47, 1731-1733.
- 2. A. Mangalum, R.J. Gilliard, J. M. Hanley, A. M. Parker, R. C. Smith, *Org. Biomol. Chem.* 2010, **8**, 5620-5627.
- **3.** S. Tekin, U. Kürüm, M. Durmus, H. G. Yagliogh, Opt. Commun. 2010, **283**, 4749-4753.