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Supporting Information

Perfluorinated Gallium Phthalocyanines Axially Grafted Black Phosphorus Nanosheets for Optical limiting

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Experimental section

1. Materials

The black phosphorus (BP) crystals (99.98%) were purchased from Nanjing XianFeng Nano Company (China) and kept in a glove box filled with Ar before use. The other analytically pure chemicals were purchased from Aladdin and used without further purification. Organic solvents were purified, dried, and distilled under dry nitrogen.

2. Measurements and Instruments

General: The ultraviolet visible near infrared (UV-Vis-NIR) absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. A HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer was used to record the steady-state fluorescence spectra. All samples for the fluorescence measurement were dissolved in dry solvent, filtered, transferred to a long quartz cell, and then capped and bubbled with dry nitrogen for 15 min. Fourier transform infrared (FTIR) spectra were performed on a Nicolet Nagma-IR 550 spectrophotometer using KBr pellets. Raman spectra were recorded on a LabRAM HR Evolution Raman spectrometer (HORIBA Scientific, France) with excitation laser beam wavelength of 532 nm. Transmission electron microscopy (TEM) images were recorded on a JEOL-2100 (JEOL Ltd., Japan) TEM system operated at 200 kV. Atomic Force Microscope (AFM) images were record on performed using a Solver P47 PRO (NT-MDT Co., Moscow, Russia) microscope. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS HSi spectrometer with a monochromatized Al KR X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. A Bruker ELEXSYS 100G-18KG/EMX-8/2.7C spectrometer in conjunction with a split-coil 6T superconducting magnet was used for W-band (95 GHz) electron paramagnetic resonance (EPR). Ultroviolet Photoelectron Spectrometer (UPS) spectrum was recorded on an Escalab 250Xi (Thermo Scientific). MALDI-TOF-MS was recorded on an Ionization Time of Flight Mass Spectrometry with Matrix-Assisted Laser Desorption (ABS, Singapore). ^{31}P NMR spectrum was recorded on an Avance III 400 MHz instrument (Bruker) and the ^{19}F NMR spectrum was recorded on an Ascend 600 MHz instrument (Bruker). The Femtosecond transient absorption (fs-TA) spectra were recorded on a HELIOS Fire Femtosecond Transient Absorption Spectrometer (Ultrafast System, USA) with the λ_{ex}=400 nm in NMP.

Molecular simulation: Molecular simulation of F_{16}PcGa-BP was carried out with the Gaussian 03 program package on a Hewlett–Packard Xeon Two Sockets Quad-Core workstation with 8 CPUs and 16 GByte memory. Molecular orbitals and their energy levels were calculated with density function theory (DFT) in B3LYP/6–31G(d) level. Vibrational frequencies were calculated analytically to ensure that the optimized geometries really correspond to the total energy minima.

NLO measurement: 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 ~60% at 532 nm.

3. Materials preparation

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, 100 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 10 hours in a water bath of 10-15^{0}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 10000 rpm for 60 minutes. The collected solid few layer BP was directly used for the synthesis of 4-HBT-BP.

Synthesis of 4-HBT-BP: A mixture of 4-hydroxybenzenediazonium-tetrafluoroborate (1000 mg), tetrabutylammonium hexafluorophosphate (1000 mg) and BP (50 mg) in anhydrous acetonitrile (100 mL) was bubbled with dry argon for 30 min and then stirred at room temperature for 24 h, followed by stirring at 50^{0}C for additional 24h. After cooling to room temperature and centrifugation, the collected solid sample was washed with acetonitrile until the filtrate is colorless, and then dried under vacuum for 12 h to give 4-HBT-BP (107 mg).

Synthesis of F_{16}PcGaCl: To a mixture of tetrafluorophthalonitrile (600 mg, 3 mmol) and 1-chloronaphthalene (10 ml) was added $GaCl_3$ (260.7 mg, 1.5 mmol) at 30^{o}C under argon. After stirring at 200°C for 5 h, the reaction mixture was allowed to cool to 150 °C and filtered at the same temperature. The achieved crude product was washed with NMP (150 ml) and methanol (150 ml), and then dried under vacuum at 60 °C for 24 h to give $F_{16}PcGaCl$ (535 mg, 79%). ^{19}F NMR (600 Hz, $CDCl_3$): δ/ppm= -140.3, -149.3; MALDI-TOF-MS: calcd for $C_{32}F_{16}N_8GaCl$: m/z=904, found: m/z=905 $[M+H]^+$, 868 $[M-Cl+H]^+$.

Synthesis of $F_{16}PcGa$-BP: A mixture of 4-HBT-BP (50 mg), $F_{16}PcGaCl$ (500 mg) and DMSO (20 mL) was sonicated for 10 min first, and then was added anhydrous K_2CO_3 (230 mg) at 110°C, followed by stirring for 12 h at the same temperature. After cooling to the room temperature, the reaction mixture was centrifuged. The achieved solid product was washed with anhydrous methanol and filtered until the filtrate is colorless. The solid obtained was thoroughly vacuum-dried at 60 °C for 24h to give 114 mg of $F_{16}PcGa$-BP.

Preparation of PMMA-based films: The sample (BP, $F_{16}PcGaCl$, and $F_{16}PcGa$-BP) in NMP was added to a cyclohexanone solution of PMMA (100 g.L^{-1}) at a partial concentration ~2 g.L^{-1}. This was followed by sonic agitation until a well-dispersed solution was formed. By using multilayer conventional spin casting technique, we achieved PMMA-based films which were further dried at 60°C for 72h under high vacuum to remove any possible residual organic solvent before NLO measurements.

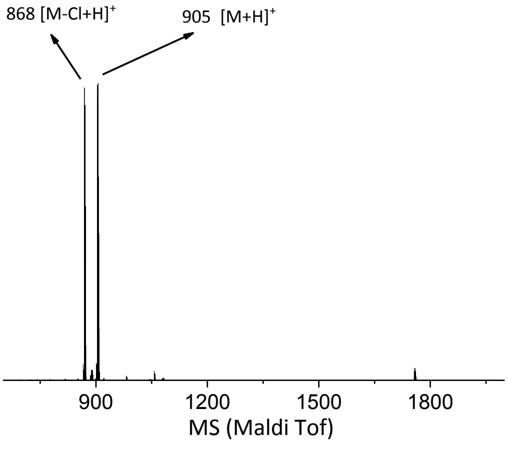

Figure S1. MALDI-TOF-MS spectrum of $F_{16}PcGaCl$.

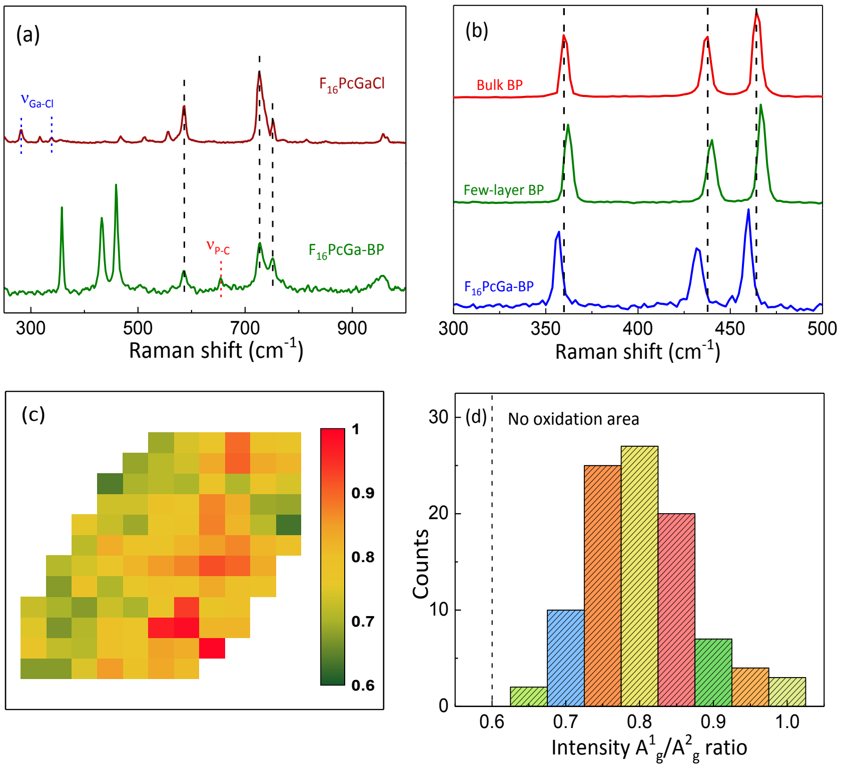

Figure S2. (a,b) Raman spectra of the samples; (c) scanning Raman microscopy mapping of F_{16}PcGa-BP depending on the $A^1{}_g$/ $A^2{}_g$ intensity ratios; and (d) $A^1{}_g$/ $A^2{}_g$ intensity ratio statistical histogram.