

Supporting Information

Fabrication and Nonlinear Optical Characterization of Fluorinated Zinc Phthalocyanine Covalently Modified Black Phosphorus/ PMMA Film Using Nanosecond Z-Scan Technique

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Experimental section

1. Materials

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. The other analytically pure chemicals were purchased from Aladdin and used without further purification. Organic solvents were purified, dried, and distilled under dry nitrogen. F₁₂NO₂PcZn was synthesized according to the literatures.^{1,2}

Preparation of PMMA-based films: The sample (BP, F₁₂NH₂PcZn, F₁₂PcZn-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 24 h under high vacuum to remove any possible residual organic solvent before NLO measurements.

2. Measurements and Instruments

The ultraviolet-visible-near infrared (UV-Vis-NIR) 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 514 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 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. Scanning electron microscope (SEM) images and Energy dispersive X-ray spectroscopy images were recorded on a Hitachi S-3400N.

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 rate was set to 2 Hz. To evaluate their NLO responses, both the dispersions and films were adjusted to have similar linear transmittances of ~57% at 532 nm.

3. Materials synthesis

3.1 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°C until a homogeneous suspension was formed. After being centrifuged at 5000 rpm for 120 minutes, the supernatant 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 F₁₂PcZn-BP.

3.2 Synthesis of F₁₂NH₂PcZn

To a stirred solution of F₁₂NO₂PcZn (837 mg, 1.0 mmol) in dry DMF (15 mL) was added Na₂S·9H₂O (2882 mg, 12.0 mmol), followed by stirring at 60 °C for 2 h. After cooling to room temperature, the reaction mixture was poured into 400 mL of deionized water and then kept at 5°C for 12 h. The solid product was collected by filtration, washed with 50 mL of HCl (1M) and 500 mL of deionized water, and freeze-dried for 24 h to give F₁₂NH₂PcZn (517 mg, 64.1%). IR: 1606 cm⁻¹ (ν_{N-H}), 1089 cm⁻¹(ν_{C-F}).

3.3 Synthesis of zinc phthalocyanine-based diazonium salt (F₁₂PcZn-N₂⁺BF₄⁻)

To a green mixture of HBF₄ (0.23 mL, 1.75 mmol, in 48 wt% H₂O), F₁₂NH₂PcZn (200 mg (0.25 mmol) and glacial acetic acid (10 mL) was dropwise added 5 mL of isoamyl nitrite in glacial acetic acid. After stirring at 15~20°C for 10 minutes, the reaction mixture was poured into 20 mL of diethyl ether and kept at -22°C for 6h. After filtration, the achieved filter cake was washed with diethyl ether (200 mL) and freeze-dried for 24h to give 215 mg of diazonium salt (95% yield). MALDI-TOF-MS: calcd for C₃₂H₃F₁₂N₈Zn⁺: m/z=791, found: m/z=792 [M+H]⁺; IR: 2240 cm⁻¹ (ν_{-N≡N}), 1089 cm⁻¹(ν_{C-F}).

3.4 Synthesis of F₁₂PcZn-BP

A mixture of F₁₂PcZn-N₂⁺BF₄⁻(100 mg) and BP (50 mg) in anhydrous DMF (100 mL) was bubbled with dry argon for 30 min and then stirred at room temperature for 24h, followed by stirring at 50°C for additional 24h. After cooling to room temperature, the reaction solution was dialyzed (molecular weight cut-off 1.0 kDa) against anhydrous DMF for 2 days during which the used DMF was replaced with the fresh DMF every 4 h, and then continued to be dialyzed with against deionized water for additional 2 days. The used water was replaced with the fresh deionized water every 4 h. The collected solid product was freeze-dried for 24 h to give dark-brown F₁₂PcZn-BP.

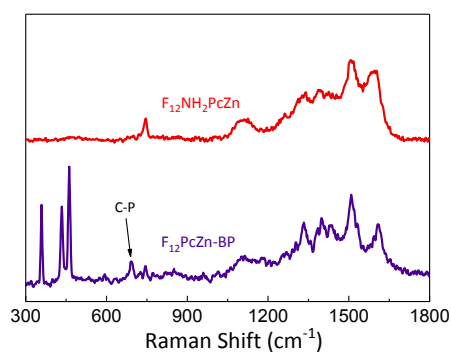


Figure S1. Raman spectra of $F_{12}NH_2PcZn$ and $F_{12}PcZn-BP$.

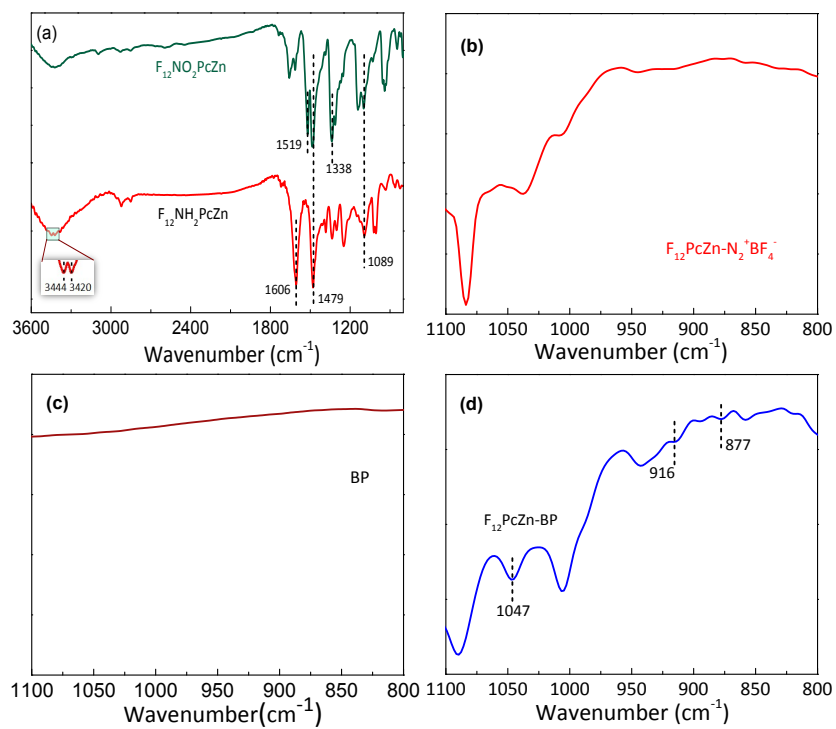


Figure S2. FTIR spectra of the samples.

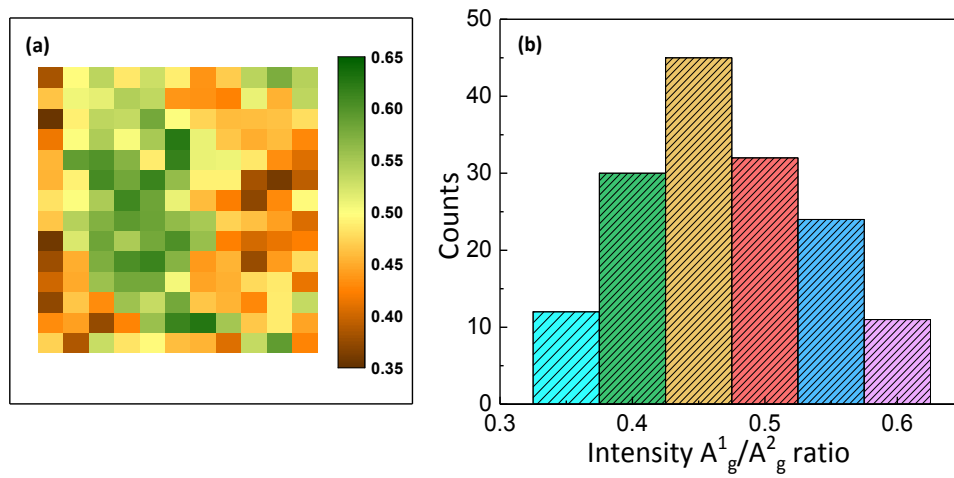


Figure S3. (a) Scanning Raman microscopy analysis of Few-layer BP after 7 days under ambient condition showing the corresponding intensity A_{1g}/A_{2g} ratio; (b) mean Raman spectra of the areas marked in (a).

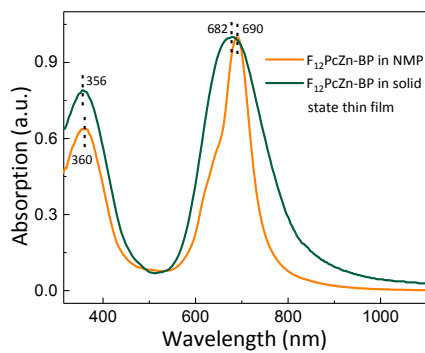


Figure S4. UV-Vis-NIR absorption spectra of the samples.

Table S1. Linear and NLO data of the film samples.

Laser	$E_I^{[a]}$ [μJ]	sample	$T_0^{[b]}$ [%]	$a_0^{[c]}$ [cm^{-1}]	$\beta_{eff}^{[d]}$ [cm/GW]	$\text{Im}\chi^{(3)[e]}$ [$\times 10^{-12}$, esu]
532 nm	25	BP/PMMA	57.34	42.91	-	-
	50	BP/PMMA	57.34	42.91	-	-
	100	BP/PMMA	57.34	42.91	-	-
	300	BP/PMMA	57.34	42.91	-	-
	400	BP/PMMA	57.34	42.91	38.57	16.47
	500	BP/PMMA	57.34	42.91	43.34	18.51
2 Hz	100	$\text{F}_{12}\text{NH}_2\text{PcZn}/\text{PMMA}$	56.73	31.08	38.80	16.57
	300	$\text{F}_{12}\text{NH}_2\text{PcZn}/\text{PMMA}$	56.73	31.08	45.26	19.33
	400	$\text{F}_{12}\text{NH}_2\text{PcZn}/\text{PMMA}$	56.73	31.08	54.47	23.26
	500	$\text{F}_{12}\text{NH}_2\text{PcZn}/\text{PMMA}$	56.73	31.08	67.87	28.98
	100	$\text{F}_{12}\text{PcZn-BP}/\text{PMMA}$	58.17	46.73	-	-
	200	$\text{F}_{12}\text{PcZn-BP}/\text{PMMA}$	58.17	46.73	151.44	64.66
	300	$\text{F}_{12}\text{PcZn-BP}/\text{PMMA}$	58.17	46.73	158.88	67.84
	500	$\text{F}_{12}\text{PcZn-BP}/\text{PMMA}$	58.17	46.73	177.10	75.62
	500	Annealed $\text{F}_{12}\text{PcZn-BP}/\text{PMMA}$	51.13	57.82	263.47	112.50

[a] E_I : input pulse energy. [b] T_0 : linear transmittance. [c] a_0 : linear absorption coefficient. [d] β_{eff} : nonlinear coefficient. [e] $\text{Im}\chi^{(3)}$: imaginary third-order susceptibility.

References

- (1) W. Sharman and J. Lier, *Bioconjugate Chem.* 2005, **16**, 1166-1175.
- (2) C. Romero-Nieto, A. Medina, A. Molina-Ontoria, C. Claessens, N. Martín, T. Torres and D. Guldi, *Chem. Commun.* 2012, **48**, 4953-4955.