

## Supporting Information

### Direct Covalent Modification of Black Phosphorus Quantum Dots with Conjugated Polymer for Information Storage

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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 argon.

##### 2. Measurements and Instruments

The number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of the polymers were determined with a Waters 2690 gel permeation chromatography (GPC) using a polystyrene standards eluting with DMF. A HITACHI U-4100 spectrophotometer was employed to measure ultraviolet/visible absorption spectra of the samples. The UV-Vis-NIR spectra of the samples were measured on the SHIMADZU UV-Vis 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 recorded using Spectrum 100 spectrophotometer (Perkin Elmer, Inc., USA). Raman spectra were recorded on an Invia/Reflrx Laser Micro-Raman spectrometer (Renishaw, England) with excitation laser

beam wavelength of 514 nm. Atomic force microscopy (AFM) and conductive atomic force microscopy (C-AFM) measurements were performed on a Solver P47-PRO (NT-MDT Co., Moscow, Russia) microscope, and a Bruker Dimension Icon scanning probe microscope, respectively. 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 K $\alpha$  radiation as X-ray source for radiation. A Bruker ELEXSYS EMX-8/2.7C spectrometer in conjunction with a split-coil 6T superconducting magnet was used for W-band (95 GHz) light-induced electron paramagnetic resonance (LEPR). These measurements were performed using an Oxford flow cryostat with a Bruker cylindrical cavity which allows optical access to the sample through an optical fiber. The results presented here are recorded with a modulation frequency and amplitude of 100 kHz and 4 G, respectively, and a microwave frequency and microwave power of 9.860 GHz and 2.006 mW. A 450 nm continuous-wave mercury-vapor lamp (5 mW·cm<sup>-2</sup>) was employed to irradiate PFCz-g-BPQDs for 3 min under ambient conditions.

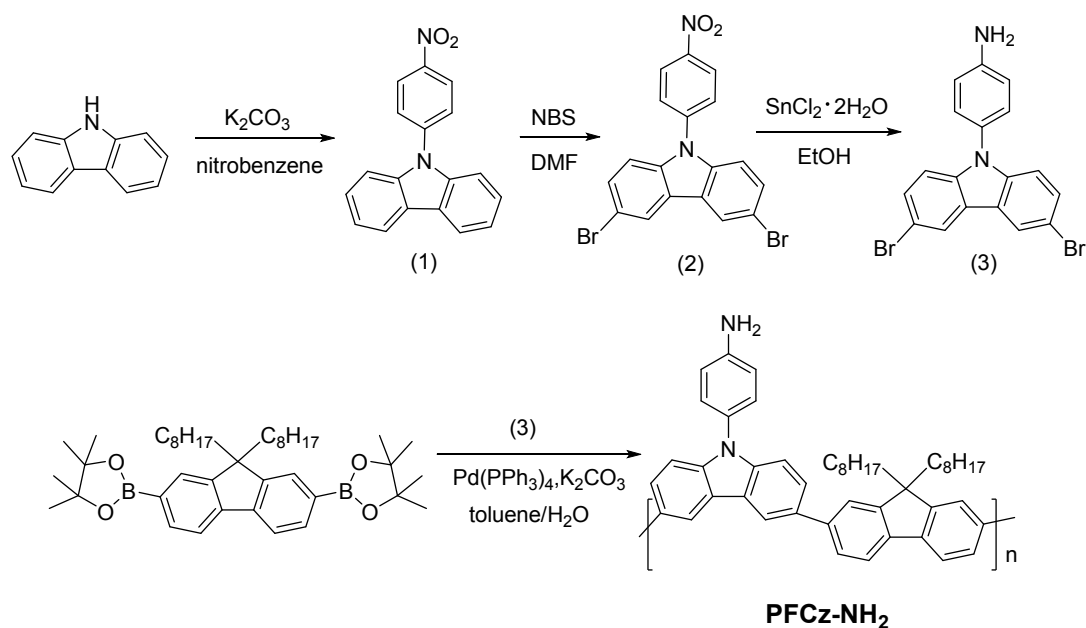
### **3. Device fabrication**

The ITO glass substrate was carefully precleaned sequentially with deionized water, acetone, and 2-propanol in an ultrasonic bath for 15 min, and then treated with oxygen plasma. A 100  $\mu$ L of PFCz-g-BPQDs solution (10 mg·mL<sup>-1</sup>) in NMP was spin-coated on the pre-cleaned ITO sheet at a spinning speed of 800 rpm for 20 s and then 1800 rpm for 60 s, followed by the removal of the solvent under vacuum at 80°C overnight. Al top electrodes were deposited on

the surface of active layer through a shadow mask at  $10^{-7}$  Torr via E-beam evaporation. All electrical measurements were performed on a Keithley 4200 semiconductor parameter analyzer in ambient condition without any device encapsulation.

## 4. Materials Synthesis

### 4.1 Synthesis of PFCz-NH<sub>2</sub>



**Scheme S1.** Synthesis process of poly[(9,9-dioctyl-9H-fluorene)-*alt*-(4-(9H-carbazol-9-yl)aniline)] (PFCz-NH<sub>2</sub>)

#### 4.1.1 Synthesis of 9-(4-nitrophenyl)-9H-carbazole (1):

A stirred DMF solution of 1-bromo-4-nitrobenzene (4.82g, 24mmol), carbazole (3.34g, 20mmol), K<sub>2</sub>CO<sub>3</sub> (2.76g, 20mmol), 1,10-phenanthridine (2.16g, 4mmol) and CuI (0.76g, 4mmol) was refluxed for 48h. After cooling to the room temperature, 100 mL of ice-water was poured into the reaction mixture. The collected yellow solid was washed with distilled water and methanol for several times, respectively, and dried at 50°C for 6h under reduced pressure. Yield: 4.9g (85%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ/ppm = 8.46 (m, 2H), 8.14 (d, 2H, J = 8 Hz), 7.78 (m, 2H), 7.49 (d, 2H), 7.44 (m, 2H), 7.34 (m, 2H); EI-MS: m/z 288.1[M<sup>+</sup>].

#### 4.1.2 Synthesis of 3,6-dibromo-9-(4-nitrophenyl)-9H-carbazole (2):

A mixture of 9-(4-nitrophenyl)-9H-carbazole (2.89g, 10mmol) and N-bromosuccinimide (NBS, 3.91g, 22mmol) was stirred in anhydrous dimethylformamide (30 mL) at 0 °C for 48 h, and then a 100 mL of ice-water was added to the above system. The collected yellow precipitate was washed several times with water and methanol, respectively, and dried at 50°C for 6 h under reduced pressure. Yield: 3.13g (70%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ/ppm = 8.51-8.49 (m, 2H), 8.21 (d, 2H), 7.76- 7.73 (m, 2H), 7.57-7.54(m, 2H), 7.34-7.32 (d, 2H). EI-MS: m/z 445.9[M<sup>+</sup>].

#### 4.1.3 Synthesis of 3,6-dibromo-9-(4-aminophenyl)-9H-carbazole (3):

A mixture of compound (2) (2.5g, 5.6mmol) and SnCl<sub>2</sub>·2H<sub>2</sub>O (6.3g, 28mmol) in EtOH (100 mL) was refluxed for 48 h. The mixture was concentrated under reduced pressure and the pH was adjusted to 9 by treatment with 10% aqueous NaOH. The mixture was extracted with toluene, the organic layers were washed several times with saturated brine and H<sub>2</sub>O, respectively, dried over anhydrous MgSO<sub>4</sub> and filtered. After removal of the solvent under reduced pressure, the solid product was recrystallized from toluene to afford the product as ivory crystals. Yield: 1.91g (82%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ/ppm = 8.17 (d, 2H), 8.47 (dd, 2H), 7.16-7.23 (m, 4H), 6.85 (d, 2H), 3.90 (br s, 2H); EI-MS: m/z 415.9[M<sup>+</sup>].

#### 4.1.4 Synthesis of PFCz-NH<sub>2</sub>:

A mixture of (3) (418 mg, 1mmol), 9,9-dioctylfluorene-2,7-bis(4,4,5,5-tetramethyl- 1,3,2-dioxaborolane) (643 mg, 1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (8 mg), K<sub>2</sub>CO<sub>3</sub> (552 mg, 4mmol), toluene (10 mL) and distilled water (2 mL) in a Schlenk tube was stirred at 80°C for 48 h. Then an excess of phenylboronic acid and bromobenzene were added as end-capping reagents sequentially in

12 h interval. The mixture was extracted with chloroform for three times, and the combined organic extracts were washed several times with water, brine, and dried over anhydrous  $\text{MgSO}_4$  and filtered. The filtrate was concentrated into a small volume. The polymer solution was added dropwise into stirred methanol. After filtration, the collected solid was purified by reprecipitating into methanol and then Soxhlet extraction with acetone. The polymer was then dried under vacuum to give a white solid (415 mg, yield 64%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta/\text{ppm} = 8.55(\text{m}, 2\text{H}), 7.3-7.9(\text{m}, 10\text{H}), 6.95(\text{s}, 4\text{H}), 3.94(\text{br s}, 2\text{H}), 2.12(\text{b}, 4\text{H}), 1.10-1.40(\text{m}, 24\text{H}), 0.76(\text{b}, 6\text{H})$ .

#### **4.2 Synthesis of $\text{PFCz-N}_2^+\text{BF}_4^-$ :**

0.20 mL (3.18 mmol) of  $\text{HBF}_4$  in 50 wt%  $\text{H}_2\text{O}$  was added to  $\text{PFCz-NH}_2$  (250 mg) under argon atmosphere, and then 20 mL of acetic acid was added into the above system. After cooling to  $-22^\circ\text{C}$ , isoamyl nitrite (0.15 mL, 1.13 mmol) in acetic acid (10 mL) was very slowly dropped into the above light-yellow solution. This reaction mixture was kept at  $-22^\circ\text{C}$  for 12 hours, followed by quenching with 20 mL of diethyl ether. The gained red solid was filtered off over a  $0.2\ \mu\text{m}$  pore filter and washed with diethyl ether for three times until the solvent is colorless. Yield: 283 mg (99%). Before use, the red  $\text{PFCz-N}_2^+\text{BF}_4^-$  solid was stored in refrigerator to avoid high temperature induced self-coupling of diazonium salts.

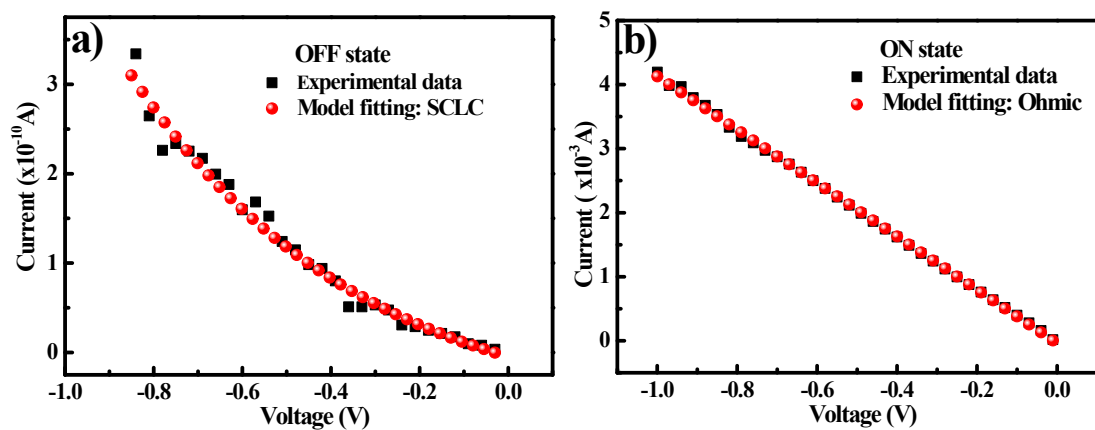
#### **4.3 Preparation of BPQDs:**

By using liquid exfoliation technique that has been widely used to exfoliate various layered-materials producing single- and/or few-layer nanosheets, we prepared BPQDs 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 150 mL of dry NMP,

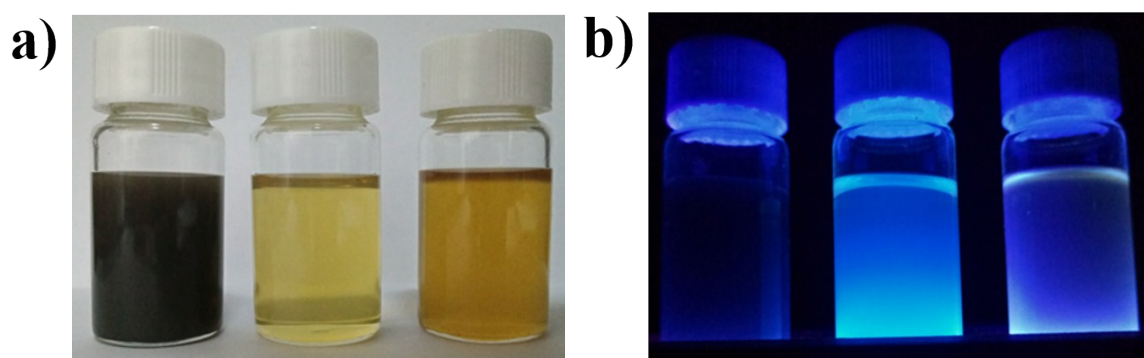
and then sonicated for 6h in an ice-bath at the power of 200W. The resultant dispersion was centrifuged for 120 min at speed of 9000 rpm. The supernatant containing BPQDs was decanted gently and kept in a dark bottle under argon atmosphere. The gained precipitate was re-dispersed in 50mL NMP, re-sonicated to produce more BPQDs. The above cyclic process was repeated for at least three times. Before use, the above BPQDs dispersions were centrifuged at high speed of 12000 rpm for 30 minutes. The collected white BPQDs solid were directly used for the synthesis of PFCz-*g*-BPQDs.

### **4.3 Synthesis of PFCz-*g*-BPQDs**

BPQDs were functionalized with PFCz-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> through a spontaneous reaction between a highly soluble diazotated polymer, PFCz-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>, and BPQDs under aqueous conditions. The obtained PFCz-*g*-BPQDs is highly soluble in common organic solvents such as toluene and DMF. In a typical reaction, a mixture of PFCz-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> (202mg) and tetrabutylammonium hexafluorophosphate (581 mg, 0.15 mmol) in acetonitrile (30 mL) was added dropwise to the stirred BPQDs (40 mg) dispersion in acetonitrile, followed by vigorously stirring for 12h. After removal of solvent by centrifuging at high speed of 12000 rpm for 15 minutes, the collected solid was physically agitated in a large volume of dry acetonitrile, and then washed with a large amount of deionized water, and dried in vacuum for 6 h to give 110 mg of dark green solid.



**Figure S1.** Experimental and fitted data of I–V characteristics for the Al/PFCz-g-BPQDs/ITO device in the OFF state (a) and the ON state (b).



**Figure S2.** a) Digital pictures of BP, BPQDs and PFCz-g-BPQDs dispersed in NMP (from left to right); b) photoluminescent images of BP, BPQDs and PFCz-g-BPQDs dispersed in NMP (from left to right) under excitation with 365 nm laser light.