Supplementary Materials for

**Regulating the reactivity of black phosphorus via protective chemistry**

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Supplementary Materials and Methods

Materials

Red phosphorus (RP), tin (Sn) and tin iodide (SnI$_4$) were purchased from Aladdin (Shanghai, China). Aluminum chloride (AlCl$_3$), 1,2-benzenedicarboxylic acid (PA), 1,2-benzenediol (BDO), 1,2-benzenedithiol (BDT), 1,2-diaminobenzene (BDA), 1-dodecanethiol (DCT), 4-nitrobenzenethio (NBT), tin chloride (SnCl$_4$), and titanium tetrachloride (TiCl$_4$) were obtained from Alfa (Shanghai, China). Hydrogen tetracholoroauric acid (HAuCl$_4$·3H$_2$O) and palladium chloride (PdCl$_2$) were purchased from Sigma-Aldrich (Shanghai, China). Ethylene diamine tetraacetic acid tetrasodium (EDTA-4Na), glutathione (GSH), silver nitrate (AgNO$_3$), and sodium citrate (SC) were obtained from Shanghai Chemical Co (Shanghai, China). Other chemicals were purchased from Xilong Scientific Co., Ltd (China). All chemicals were used without further purification.

Methods

Preparation of Bulk BP. Bulk BP was prepared according to the literature (21). In a typical synthesis, RP (500 mg), Sn (20 mg), and SnI$_4$ (10 mg) were sealed in a quartz tube. The tube was heated to 923 K with a heating ramp rate of about 1.35 K per min and after keeping at 923 K for five hours. Then the temperature was reduced to 773 K at a cooling rate of 0.33 K per min, followed with a natural cooling process. The large BP crystals were collected and washed with hot toluene and acetone for several times to remove the residual mineralizer. After being dried under vacuum, the product was kept in a glovebox for further analysis.

Preparation of BP. BP nanosheets were prepared using a simple liquid exfoliation technique. In brief, bulk BP (20 mg) was dispersed in DMF (40 mL) that was bubbled with argon to eliminate the dissolved oxygen for avoiding the oxidation. The solution was sonicated in ice water for 20 h. Then, the resultant brown suspension was centrifuged at 2000 rpm for 20 min to remove the residual unexfoliated BP. BP nanosheets were collected from the supernatant by centrifugation at 12000 rpm for 20 min.

Detection of PO$_4^{3-}$ by Ammonium Molybdate Spectrophotometric Method (21).

Solution A - H$_2$SO$_4$ solution (H$_2$SO$_4$:H$_2$O = 1:1)
Solution B - K$_2$S$_2$O$_8$ solution (50 g/L)
Solution C - Vitamin C solution (100 g/L)
Solution D - Molybdate solution
   (NH$_4$)$_6$Mo$_7$O$_{24}$.4(H$_2$O) (0.13 g/mL 100 mL) solution and C$_8$H$_4$K$_2$O$_{12}$Sb$_2$ (0.0035g/mL 100 mL) are slowly added to the 300 ml solution A.
Solution E - K$_2$HPO$_4$ solution (2 μg/mL)
In this paper, PO$_4^{3-}$ was detected via ammonium molybdate spectrophotometric method. PO$_4^{3-}$ reacts with NH$_4^+$MoO$_4^{2-}$ to form (MoO$_2$-4MoO$_3$)$_2$H$_3$PO$_4$ under acidic condition (Vitamin C as reducing agent). The absorption peak is at 710 nm, which is a characteristic absorption of (MoO$_2$-4MoO$_3$)$_2$H$_3$PO$_4$.

\[
\text{PO}_4^{3-}(\text{E}) + \text{NH}_4^+\text{MoO}_4^{2-}(\text{D}) + \text{H}^+ \rightarrow (\text{NH}_4)_3\text{PO}_4\cdot12\text{MoO}_3+\text{H}_2\text{O}
\]

\[
(\text{NH}_4)_3\text{PO}_4\cdot12\text{MoO}_3+\text{Vitamin C solution (C)} + \text{H}^+ \rightarrow (\text{MoO}_2\cdot4\text{MoO}_3)_2\text{H}_3\text{PO}_4
\]

Standard curve (absorption intensity at 710 nm v.s. PO$_4^{3-}$ concentration):

The linear detection range for PO$_4^{3-}$ spanned a concentration range of 0.01~0.8 μg/mL. E solutions (K$_2$HPO$_4$ 10 mL; 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6 and 0.8 μg/mL) were prepared, respectively. B solution (K$_2$S$_2$O$_8$, 2 mL) was added to each E solution (K$_2$HPO$_4$) for phosphite oxidation to phosphate and then each E solution (K$_2$HPO$_4$) was heated at 120 °C for 30 min in an autoclave, respectively. After cooling down to room temperature, C solution (vitamin C, 1 mL) and D solution (molybdate, 2 mL) were subsequently added to each E solution (K$_2$HPO$_4$). After 15 min, the UV-vis of mixed solution was measured and the absorbance of 710 nm corresponds to amount of PO$_4^{3-}$ (as shown Fig. S5).

Amount of PO$_4^{3-}$ in BP and BP/Al$^{3+}$/BDT aqueous solution were detected via this method. The BP (7 μg/mL) and BP/Al$^{3+}$/BDT (7 μg/mL) dispersed in water for different periods of time were centrifuged at 15000 rpm for 20 min to collect the supernatant, respectively. Each supernatant (1 mL) collected was diluted to ten folds to meet the detection range of 0.01~0.6 μg/mL. Then, amount of PO$_4^{3-}$ of supernatants were determined by the standard curve respectively.

**Detection of Al$^{3+}$ via Fluorescent photometry with 8-hydroxyquinoline (42).**

Solution A - 2% 8-hydroxyquinoline (8-HQ) solution: acetic acid solution of 8-HQ (0.33 g/mL 6 mL) was diluted to 1000 mL distilled water.

Solution B - CH$_3$COONH$_4$-NH$_3$.H$_2$O (NH$_4$Ac-NH$_3$.H$_2$O) buffer solution.

Solution C - KAl(SO$_4$)$_2$·12H$_2$O (2.00 μg/mL).

In this paper, Al$^{3+}$ was detected via fluorescent photometry with 8-HQ. Al$^{3+}$ reacts with 8-HQ to form 8-hydroxyquinoline aluminum salt (Alq$_3$). The emission peak at 510 nm under the excitation wavelength of 365 nm is a characteristic peak of Alq$_3$. 

![8-HQ + Al$^{3+}$](image)
Standard curve (emission peak at 510 nm v.s. Al\(^{3+}\) concentration):

\[
\text{KAl(SO}_4\text{)}_2\cdot12\text{H}_2\text{O} \quad \text{(2.00} \ \mu\text{g/mL; 0, 0.2, 0.4, 0.6, 0.8, and 1 mL)} \quad \text{was diluted to 10~20 mL in the separating funnel, respectively. Then, A solution (8-HQ, 1 mL) and B solution (NH}_4\text{Ac-NH}_3\cdot\text{H}_2\text{O buffer, 1 mL) were added to C solution (KAl(SO}_4\text{)}_2\cdot12\text{H}_2\text{O} \quad \text{in turn. Each solution was extracted twice with 5 mL chloroform, and the extraction of chloroform was diluted to 10 mL. The photoluminescence (PL) of the mixed solution was measured under the excitation wavelength of 365 nm at room temperature, and the emission of 510 nm corresponds to amount of Alq3, namely amount of Al}\(^{3+}\). The linear detection range for Al\(^{3+}\) spanned a concentration range of 0.002~0.24 \ \mu\text{g/mL.}
\]

The BP/Al\(^{3+}\)/BDT (20 \ \mu\text{g/mL}) was dispersed in EDTA-4Na aqueous solution. Then, the mixed solution was centrifuged at 15000 rpm for 5 min to remove supernatant. The precipitates were re-dispersed in 10~20 mL water, and the amount of Al\(^{3+}\) on the BP surface was detected via Fluorescent photometry with 8-HQ.

**Preparation of BP, BP/Al\(^{3+}\)/BDT and Deprotected BP/Al\(^{3+}\)/BDT Films.** BP (4 mg) was dispersed in 25 mL alcohol solution under the assistance of ultrasonic bath. The dispersed mixture was deposited on a commercial hydrophilic poly(vinylidene fluoride) (PVDF) membrane (diameter = 4 cm) under vacuum. After being dried under vacuum, the film was kept in a glovebox for further analysis. The fabrication of BP/Al\(^{3+}\)/BDT film and deprotected BP film followed the same procedure.

**Solar Vapor Generation.** The fabricated circular BP based film with a diameter of \(\approx 1.6 \ \text{cm} \ (0.64 \ \text{mg BP/Al}^{3+}/1.2\text{-BDT}) \) was used for solar steam-generation tests. The simulated solar irradiation was provided using a solar simulator (CEL-HXF300) with a light density of 1 kW/m\(^2\) (1 sun). The sample evaporator was floated on a 5 mL beaker filled with 5% NaCl H\(_2\)O solution, and the evaporation rates were measured for 60 min at steady-state condition. The weight loss over the entire process was recorded using an electronic mass balance.

**Characterizations.** Fourier transform infrared spectrometer (FTIR) was measured using NICOLET iS10, and \(^1\)H NMR spectra of IL-NH\(_2\), ImPPO and BPPO were recorded on an Avance II 500 MHz (Bruker, Switzerland) using CDCl\(_3\) as the solvents. The micrographs of samples were taken using transmission electron microscope (TEM, JEOL JEM-2100), high resolution TEM (HRTEM, TECNAI-F-30), transmission-reflecting polarizing microscope (ECLIPSE/Ci-S, Nikon), and scanning electron microscopy (SEM, SU70, Hitachi). The high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image was acquired on a JEOL JEM ARM 200F under 80 kV. Atomic force microscope (AFM) images were recorded using an atomic force microscope (DI Multimode V/DI Multimode V, Veeco) in tapping mode. X-Ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 (USA). Powder X-ray diffraction (XRD) patterns were collected from Philips X’Pert Pro (Philips, Amsterdam, Netherlands; \(\lambda = 1.54056 \ \text{Å}\)) using Cu Ka radiation. The optical properties of
nanoparticles were characterized by a UV-visible spectrophotometer (UV-2550, Shimadzu) and a photoluminescence spectrophotometer (Hitachi F7000, Japan). Thermogravimetric analysis (TGA) was performed on an SDT-Q600 instrument under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Raman spectra (XploRA, Jobin-Yvon) were recorded with a solid-state laser at the excitation wavelength of 532 nm. Zeta potential analysis was performed using a Malvern Nano-ZS. The current-voltage curves were collected from CHI440C.

**Conductivity Measurements.** Conductivity measurements of BP, BP/Al³⁺/BDT and deprotected BP/Al³⁺/BDT were conducted as follows: the aqueous solution of samples was dropped onto the glass substrates, and dried in vacuum at 60 °C for 1 h. Then, the current-voltage curves were generated via cyclic voltammetry using CHI440C (Initial E (V) = -1, High E (V) = 1, Low E (V) = -1, Scan Rate (V/s) = 0.1, Sensitivity (A/V) = 1e⁻⁵).
Fig. S1. Characterization of bulk BP and BP. SEM images of as-prepared bulk BP with (a) low and (b) high magnification. (c) XRD patterns of as-prepared bulk BP and bar diagram for the JCPDS of BP. (d) SEM, (e) TEM and (f) HRTEM images of BP. (g) AFM image of BP and height profile (inset) along the white line. (h) XRD patterns of bulk BP and BP nanosheets. (i) Raman spectra of the bulk BP and BP nanosheets.
Supplementary Note 1. The choice of metal ions

Metal ions can be divided into noble metal ions (Au$^{3+}$, Ag$^{+}$, and Pd$^{2+}$), heavy metal ions (Cu$^{2+}$, Zn$^{2+}$, Ni$^{+}$, Co$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, and Sn$^{4+}$), and light metal ions (Na$^{+}$, K$^{+}$, Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$, and Ti$^{4+}$) in the exclusion of toxic metal ions (Cr$^{3+}$, Cd$^{2+}$, and Hg$^{2+}$). For noble metal ions, BP/noble metal ions can form a redox pair, allowing spontaneous electron transfer from BP to noble metal ions. The reaction between noble metal ions and BP leads to the formation of noble metal nanoparticles (NPs) on the surface of BP (Fig. S2). For heavy and light metal ions, most of them have very weak ability to passivate BP (Fig. S2). In addition, we found TiO$_2$ and SnO$_2$ can be formed on the BP surface due to fast hydrolysis of Ti$^{4+}$ and Sn$^{4+}$ ions under ambient condition, which is not applicable for regulating reactivity of BP. Due to the electron withdrawing ability increases with decreasing of the ion radius, Al$^{3+}$ ions have a greater electron withdrawing ability relative to Ga$^{3+}$ and In$^{3+}$ (Fig. S3).

The BP/Au, BP/Pd and BP/Ag were obtained by mixing BP with HAuCl$_4$ (1 mmol/L), H$_2$PdCl$_4$ (1 mmol/L) and AgNO$_3$ (1 mmol/L) solution for 10 min (Fig. S2a-c). The obtained product was washed by ethanol and water for several times, and further characterized. TEM image shows that Au NPs (Fig. S2a), Pd NPs (Fig. S2b) and Ag NPs (Fig. S2c) are decorated on the surface of BP. In addition, the color of the solution was changed from light brown (BP) to purple (BP/Au), light black (BP/Pd) and dark brown (BP/Ag), respectively (Fig. S2d). In Fig S2e, UV-vis spectra of BP/Au and BP/Ag show peak at 530 and 406 nm, attributing to the typical surface plasmon resonance absorption of Au and Ag NPs. The results indicate Au, Pd and Ag NPs can grow on the BP surface spontaneously after immersing in HAuCl$_4$ (1 mmol/L), H$_2$PdCl$_4$ (1 mmol/L) and AgNO$_3$ (1 mmol/L) solution for 10 min, respectively. XRD patterns further support that Au, Pd and Ag NPs grow on BP (Fig. S2f). Degradation of BP/Au (Fig. S2g), BP/Pd (Fig. S2h) and BP/Ag (Fig. S2i) was studied in ambient conditions via TEM. The results show the surface of BP was oxidized significantly after one day ambient exposure. In summary, noble metal ions (HAuCl$_4$, H$_2$PdCl$_4$, and AgNO$_3$) are incapable of protecting BP.

As shown in Fig. S2k, TEM images display that surface of BP/Na$^{+}$, BP/K$^{+}$, BP/Mg$^{2+}$, BP/Ca$^{2+}$, BP/Cu$^{2+}$, BP/Zn$^{2+}$, BP/Ni$^{2+}$, BP/Co$^{2+}$, BP/Mn$^{2+}$ and BP/Fe$^{2+}$ is oxidized obviously after ambient exposure for 1 day or 2 days.

BP/Al$^{3+}$, BP/Ti$^{4+}$ and BP/Sn$^{4+}$ were obtained by simple mixing of BP and AlCl$_3$, TiCl$_4$ and SnCl$_4$ in ethanol solution, respectively (Fig. S3a-c). However, BP/Ti$^{4+}$ and BP/Sn$^{4+}$ can turn into BP/TiO$_2$ and BP/SnO$_2$ after 2 h. TEM images of BP/Al$^{3+}$ (Fig. S3a) show perfectly clean and flat surface, and no Al$_2$O$_3$ is observed on BP surface. However, TiO$_2$ and SnO$_2$ nanoparticles are observed on BP surface, as shown in Fig. S3b,c. Optical photographs (Fig. S3d inset) and zeta potentials (Fig. S3d) show poor dispersity of BP/TiO$_2$ and BP/SnO$_2$ in aqueous solution, while BP and BP/Al$^{3+}$ form homogeneous solution. In addition, XRD pattern of BP/TiO$_2$ shows the presence of both BP (JCPDS card no. 73-1358) and TiO$_2$ (JCPDS card no. 21-1236) phase (45). Similarly, XRD pattern of BP/SnO$_2$ also gives both BP and SnO$_2$ (JCPDS card no. 50-1429) phase (46). The results verify that Ti$^{4+}$ and Sn$^{4+}$ ions can form TiO$_2$ and SnO$_2$ on the surface of BP via hydrolysis.
In addition, the effect of ion charge and ionic radii on interactions strength between mental ions and BP are further discussed (Fig. S3h-k). Li\(^+\), Mg\(^{2+}\), and Al\(^{3+}\) ions have similar radii (Li\(^+\): 60 pm, Mg\(^{2+}\): 65pm, Al\(^{3+}\): 50 pm) and different valence states. BP/Li\(^+\), BP/Mg\(^{2+}\), and BP/Al\(^{3+}\) are obtained by simple mixing of BP and corresponding metal salts (LiCl, MgCl\(_2\), AlCl\(_3\)) in ethanol solution at room temperature. The surface compositions in BP/Li\(^+\), BP/Mg\(^{2+}\), and BP/Al\(^{3+}\) samples are analyzed via XPS. No Li and Mg signals are found in the BP/Li\(^+\) and BP/Mg\(^{2+}\) samples (Fig. S3h), suggesting that Li\(^+\) and Mg\(^{2+}\) cannot be modified on the surface of BP. XPS spectra confirm that Al\(^{3+}\) is easily modified to the surface of BP. Such results suggest that the larger the ionic charge, the stronger the interaction strength between metal ions and BP. This is because the ionic charge has high correlation with the electron withdrawing ability (47). In addition, Al\(^{3+}\), Ga\(^{3+}\), and In\(^{3+}\) ions have same valence states and different radii (Al\(^{3+}\): 50 pm, Ga\(^{3+}\) 62 pm, In\(^{3+}\): 81 pm). Obviously, Al\(^{3+}\), Ga\(^{3+}\), and In\(^{3+}\) ions are easily modified to the surface of BP (Fig. S3j). Since the electron withdrawing ability increases with the decrease of the ion radius (48), in P 2p core-level XPS spectrum, the positions of P 2p\(_{3/2}\) and P 2p\(_{1/2}\) doublet for BP/Al\(^{3+}\) (130.2 and 131.2 eV), BP/Ga\(^{3+}\) (130.1 and 131.0 eV), BP/In\(^{3+}\) (129.8 and 130.8 eV) sequentially move in the direction of low binding energy, suggesting the interaction strength between metal ions and BP gradually decreases.

The polarizing microscope images show that surface of BP/Al\(^{3+}\) remains almost unchanged after 20 days ambient exposure, and the corresponding TEM images of BP/Al\(^{3+}\) exhibit the same 2D BP nanosheet structures without observed defects (Fig. S3l).
**Fig. S2. Screening of noble metal, heavy metal and light metal ions.** TEM images of (a) BP/Au, (b) BP/Pd and (c) BP/Ag complex. (d) Optical photographs of BP, BP/Au, BP/Pd and BP/Ag. (e) UV-vis spectra of BP, BP/Au, BP/Pd and BP/Ag. (f) XRD patterns of BP, BP/Au, BP/Pd, and BP/Ag. TEM images of (g) BP/Au, (h) BP/Pd and (i) BP/Ag complex after ambient exposure for 1 day. TEM images of (k₁) BP/Na⁺, (k₂) BP/K⁺, (k₃) BP/Mg²⁺, (k₄) BP/Ca²⁺, (k₅) BP/Cu²⁺, (k₆) BP/Zn²⁺, (k₇) BP/Ni²⁺, (k₈) BP/Co²⁺, (k₉) BP/Mn²⁺, and (k₁₀) BP/Fe²⁺ after 1 day or 2 days ambient exposure. Photo Credit: Xiao Liu, Xiamen University.
Fig. S3. Characterization of BP/Al$^{3+}$, BP/TiO$_2$, BP/SnO$_2$, BP/Li$^+$, BP/Mg$^{2+}$, BP/In$^{3+}$ and BP/Gd$^{3+}$. TEM images of (a) BP/Al$^{3+}$, (b) BP/TiO$_2$, and (c) BP/SnO$_2$. (d) Zeta potentials of BP, BP/Al$^{3+}$, BP/TiO$_2$ and BP/SnO$_2$ (Inset: corresponding optical photograph). (e) XRD patterns of BP, BP/Al$^{3+}$ and Al$_2$O$_3$. (f) XRD patterns of BP, BP/TiO$_2$ and TiO$_2$. (g) XRD patterns of BP, BP/SnO$_2$ and SnO$_2$. (h) HR-XPS spectra of Li 1s for BP/Li$^+$, HR-XPS spectra of Mg 2p for BP/Mg$^{2+}$, and HR-XPS spectra of Al 2p for BP/Al$^{3+}$. (i) HR-XPS spectra of P 2p for BP/Li$^+$, BP/Mg$^{2+}$ and BP/Al$^{3+}$. (j) HR-XPS spectra of In 3d for BP/In$^{3+}$, HR-XPS spectra of Ga 2p for BP/Ga$^{3+}$, and HR-XPS spectra of Al 2p for BP/Al$^{3+}$. (k) HR-XPS spectra of P 2p for BP/In$^{3+}$, BP/Ga$^{3+}$ and BP/Al$^{3+}$. (l) Polarizing microscope images of BP/Al$^{3+}$ (0 day, 10 day, and 20 days). Photo Credit: Xiao Liu, Xiamen University.
Supplementary Note 2. The choice of hydrophobic molecule layer on BP surface

Hydrophobic molecule layer is self-assembled on the surface of BP/Al\(^{3+}\) to isolate BP from oxygen/water. Several types of molecules, typically BDT (-SH group), BDA (-NH\(_2\) group), BDO (-OH group), and PA (-COOH group), are selected for making comparison (see molecular structure in Fig. S4a-d). PA (-COOH) and BDO (-OH) molecules have strong coordination ability with Al\(^{3+}\) ions, which break the bond between BP and Al\(^{3+}\) ions. Based on the theory of soft and hard acid, Al\(^{3+}\) ion, one of the typical hard acids, has strong coordination ability with hard base (for example: -COOH and -OH group). Therefore, in the presence of -COOH and -OH group, Al\(^{3+}\) ions are linked to COOH or -OH, and cannot bind with BP (see the following part for details). On the other hand, -NH\(_2\) group and -SH group are both soft base. They can form coordinated bond with BP/Al\(^{3+}\).

BP/Al\(^{3+}\)/PA, BP/Al\(^{3+}\)/BDO, BP/Al\(^{3+}\)/BDA and BP/Al\(^{3+}\)/BDT are obtained by simply mixing BP/Al\(^{3+}\) and PA, BDO, BDA and BDT in ethanol solution, respectively (Fig. S4a-d). The structure of BP/Al\(^{3+}\)/small-molecule complex was studied by FTIR. As shown in Fig. S4a,b, there are no small-molecule characteristic bands in the FTIR spectra of BP/Al\(^{3+}\)/PA and BP/Al\(^{3+}\)/BDO, which is the same as the FTIR spectra of BP. However, the FTIR spectra of BP/Al\(^{3+}\)/BDA and BP/Al\(^{3+}\)/BDT show three and four characteristic bands, respectively (Fig. S4c,d). The characteristic bands at the position of ~3400 and ~1637 cm\(^{-1}\) are assigned to the O-H in the FTIR spectra of BP/Al\(^{3+}\)/BDA and BP/Al\(^{3+}\)/BDT. The other characteristic bands are accredited to the BDA and BDT molecule, respectively. Such results suggest that only BDT or BDA can be self-assembled on BP/Al\(^{3+}\) surface.

Water contact angles and zeta potentials further support the existence of BDT and BDA on BP/Al\(^{3+}\) surface (Fig. S4f,g). Assembly of BDT and BDA increases the contact angle of BP surface from 24.8\(^{\circ}\) to 130.5\(^{\circ}\) (BP/Al\(^{3+}\)/BDT) and 80.3\(^{\circ}\) (BP/Al\(^{3+}\)/BDA), respectively. However, the contact angles of BP/Al\(^{3+}\)/BDO (17.8\(^{\circ}\)) and BP/Al\(^{3+}\)/PA (15.3\(^{\circ}\)) are similar to that of BP (12.3\(^{\circ}\)). In addition, zeta potentials of BP/Al\(^{3+}\)/BDT and BP/Al\(^{3+}\)/BDA increase from -27.6 (zeta potentials of BP) to +29.9 and +21.0 due to Al\(^{3+}\) ions on the BP surface, respectively. Zeta potentials of BP/Al\(^{3+}\)/PA (-27.4) and BP/Al\(^{3+}\)/BDO (-26.8) are similar to that of BP (-27.6), indicating the unsuccessful binding of PA or BDO on the surface of BP.

The effect of n-alkane and aromatic ligands on self-assembled film was discussed in Fig. S4e. There are no DCT molecule characteristic bands in the FTIR spectra of BP/Al\(^{3+}\)/DCT (Fig. S4e), suggesting the absence of DCT molecule on BP/Al\(^{3+}\) surface, which is further supported by water contact angles and zeta potentials (Fig. S4f,g).

XRD pattern of BP/Al\(^{3+}\)/BDT gives the same feature peaks as that of the original BP, indicating the unchanged crystal structure (Fig. S4h). Conductivity of BP is also preserved after the protective treatment (Fig. S4i). As shown in Fig. S4j, three Raman peaks at 362.1 cm\(^{-1}\), 438.8 cm\(^{-1}\), and 468.4 cm\(^{-1}\) are observed from the BP/Al\(^{3+}\)/BDT, which can be assigned to the \(A^1_{g}\), \(B_{2g}\) and \(A^2_{g}\) modes of BP (21). Similarly, such peaks are also observed in Raman spectrum of BP. In addition, the rest of the peaks (labelled with square) is attributed to BDT molecule (49).
**Fig. S4. Characterization of BP/Al\textsuperscript{3+}/hydrophobic molecule complex.** (a) FTIR spectra of BP, BP/Al\textsuperscript{3+}, BP/Al\textsuperscript{3+}/PA and PA. (b) FTIR spectra of BP, BP/Al\textsuperscript{3+}, BP/Al\textsuperscript{3+}/BDO and BDO. (c) FTIR spectra of BP, BP/Al\textsuperscript{3+}, BP/Al\textsuperscript{3+}/BDA and BDA. (d) FTIR spectra of BP, BP/Al\textsuperscript{3+}, BP/Al\textsuperscript{3+}/BDT and BDT. (e) FTIR spectra of BP, BP/Al\textsuperscript{3+}, BP/Al\textsuperscript{3+}/DCT and DCT. (f) Zeta potentials and (g) water contact angles of BP, BP/Al\textsuperscript{3+}, BP/Al\textsuperscript{3+}/BDT, BP/Al\textsuperscript{3+}/BDA, BP/Al\textsuperscript{3+}/BDO, BP/Al\textsuperscript{3+}/PA, and BP/Al\textsuperscript{3+}/DCT, respectively. (h) XRD patterns, (i) conductivity, and (j) Raman spectra of BP and BP/Al\textsuperscript{3+}/BDT.
Supplementary Note 3. Calculating the ratio of BP/Al\(^{3+}\)/BDT.

In Fig. S5a, there are 400 phosphorus atoms in monolayer BP sheet (10 unit cell \(\times\) 10 unit cell), and the corresponding area is 14.55 nm\(^2\). Hence, there are 274900 phosphorus atoms in monolayer BP sheet (100 \(\times\) 100 nm\(^2\)). We assume that the size of BP sheet is one hundred nanometers, and the number of layers is 6. Based on the schematic illustration of BP/Al\(^{3+}\)/BDT (Fig. S5b), we deduce that 3 P atoms correspond to one Al atom and 2 Al atoms correspond to one BDT molecule. \((N_A = \text{Avogadro's constant})\). Hence, the mass of BP, Al and BDT are calculated as shown below.

Mass of phosphorus element: \(274900 \times 6 \times 31/N_A \approx 51 \times 10^6/N_A\)
Mass of aluminum element: \(274900/3 \times 2 \times 27/N_A \approx 4.9 \times 10^6/N_A\)
Mass of BDT molecule: \(274900/3/2 \times 2 \times 142.24/N_A \approx 12.9 \times 10^6/N_A\)
Mass ratio of BP:Al:BDT was calculated to be about 10:1:3, which is in agreement with the TGA results as Fig. 2i.

In addition, mass ratio of BP:Al:BDT is directly affected by the layers number of BP. By tuning the speed of centrifugation (2000 rpm, 4000 rpm and 8000 rpm), three batch of exfoliated BP with \(~2.9\) nm (6 layers), \(~12.5\) nm (24 layers) and \(~21.2\) nm (42 layers) in thickness are obtained, respectively (Fig. S5c). As the number of layers increases, the mass ratio of BP:Al:BDT is calculated to be about \(40:1:3\) (BP-4000 sample: 24 layers) and \(70:1:3\) (BP-2000 sample: 42 layers), respectively.

Preparation details (BP with different thickness): Firstly, the stock solution was centrifuged at 1000 rpm for 20 min, and the precipitate was removed. The remaining supernatant was centrifuged at 2000 rpm for 20 min, and the precipitate was collected, which named as BP-2000. Then, the supernatant collected from BP-2000 was further centrifuged at 4000 rpm for 20 min, and the precipitate was collected, which named as BP-4000. Lastly, the supernatant collected from BP-4000 was further centrifuged at 8000 rpm for 20 min, and the precipitate was collected, which named as BP-8000.
Fig. S5. Long term stability study of BP/Al\textsuperscript{3+}/BDT. (a,b) Schematic illustration for the structure of BP/Al\textsuperscript{3+}/BDT. (a) Model of BP unit cell and monolayer BP sheet (10 unit cell \times 10 unit cell). (b) Side view of the BP/Al\textsuperscript{3+}/BDT. (c) AFM images of BP with different thickness. (d) Characterization of the BP/Al\textsuperscript{3+}/BDT after ambient exposure for 12 months. (d\textsubscript{1}) TEM image, (d\textsubscript{2}) HR-TEM image, (d\textsubscript{3}) XRD, (d\textsubscript{4}) Raman spectra, and (d\textsubscript{5}) zeta potentials of BP/Al\textsuperscript{3+}/BDT (Inset: corresponding water contact angles). (e,f) UV-vis spectra addressing the BP degradation in aqueous solution. (e\textsubscript{1}) UV-vis absorption spectra of BP aqueous solution with different concentration. (e\textsubscript{2}) Plot of UV-vis absorbance at 470 nm as a function of BP concentration. (e\textsubscript{3}) Optical photograph of BP aqueous solution with different concentrations. (f\textsubscript{1}) UV-vis absorption spectra of different concentration PO\textsubscript{4}\textsuperscript{3-} aqueous solution (by ammonium molybdate spectrophotometric method). (f\textsubscript{2}) Plot of absorbance at 710 nm as a function of PO\textsubscript{4}\textsuperscript{3-} concentration. (f\textsubscript{3}) Optical photograph of PO\textsubscript{4}\textsuperscript{3-} aqueous solution with different concentrations. UV-vis absorption of PO\textsubscript{4}\textsuperscript{3-} in supernatant of (g) BP and (h) BP/Al\textsuperscript{3+}/BDT aqueous solution with different incubation durations (by ammonium molybdate spectrophotometric method). Inset: variation of the absorption ratios at 710 nm (A/A\textsubscript{1})
of $\text{PO}_4^{3-}$ ($A_i$: final value). (i,j) Reactivity study of BP and BP/Al$^{3+}$/BDT in strong oxidant-containing solution. (i) Variation of the UV-vis absorption ratios at 470 nm ($A/A_0$) of BP ($A_0$: original value), and variation of the absorption ratios at 710 nm ($A/A_i$) of $\text{PO}_4^{3-}$ ($A_i$: final value) when BP is dispersed in HAuCl$_4$, H$_2$PdCl$_4$ and AgNO$_3$ aqueous solution. (j) Variation of the absorption ratios at 470 nm ($A/A_0$) of BP/Al$^{3+}$/BDT ($A_0$: original value) and variation of the absorption ratios at 710 nm ($A/A_i$) of $\text{PO}_4^{3-}$ ($A_i$: final value) when BP and BP/Al$^{3+}$/BDT are dispersed in HAuCl$_4$, H$_2$PdCl$_4$ and AgNO$_3$ water solution. Photo Credit: Xiao Liu, Xiamen University.
Fig. S6. Characterization of BP/Al\textsuperscript{3+}/hydrophobic molecule complex. (a) FTIR spectra of BP/Al\textsuperscript{3+}/BDT and BDT. (b) FTIR spectra of BP/Al\textsuperscript{3+}/NAT and NAT. (c) FTIR spectra of BP/Al\textsuperscript{3+}/BDT+NAT, BDT and NAT. UV-vis spectra of (d) BP/Al\textsuperscript{3+}/BDT, (e) BP/Al\textsuperscript{3+}/NAT and (f) BP/Al\textsuperscript{3+}/BDT+NAT aqueous solution with different incubation durations (Inset: corresponding water contact angles). Schematic illustration of (g) BDT dense array, (h) NAT dense array, and (i) BDT and NAT hybrid array on the substrate.
Fig. S7. Characterization of the deprotected BP/Al\(^{3+}\)/BDT. (a) PL emission spectra of the solution containing different concentration of Al\(^{3+}\) (by fluorescent photometry with 8-HQ). (b) Plot of absorbance at 510 nm as a function of Al\(^{3+}\) concentration. (c) Plot of ln (\(C/C_0\)) as a function of EDTA\(-4\)Na immersing time when BP/Al\(^{3+}\)/BDT is immersed into 1 mmol/L EDTA\(-4\)Na solution, 2 mmol/L EDTA\(-4\)Na solution, 3 mmol/L EDTA\(-4\)Na solution, 4 mmol/L EDTA\(-4\)Na solution, and 5 mmol/L EDTA\(-4\)Na solution, respectively (\(C_0\) and \(C_t\) refer to the loading concentration of Al\(^{3+}\) in BP/Al\(^{3+}\)/BDT at immersion time of \(0\) and \(t\), respectively). (d) XPS spectra of BP, SC-deprotected, and GSH-deprotected BP/Al\(^{3+}\)/BDT. HR-XPS spectra of (e) P 2p and (f) Al 2p and S
2p. (g) Zeta potentials of BP, BP/Al$^{3+}$/BDT and deprotected BP/Al$^{3+}$/BDT (Inset: corresponding water contact angles). (h) XRD patterns, (i) Raman spectra and (j) conductivity of BP and deprotected BP/Al$^{3+}$/BDT. (k) Photothermal heating curves of BP (5 ppm, 10 ppm, 20 ppm) and deprotected BP/Al$^{3+}$/BDT (5 ppm, 10 ppm, 20 ppm) dispersed in water using the 808 nm laser as the irradiation source.
Fig. S8. Stability study of the deprotected BP/Al\(^{3+}\)/BDT with different amount of residual Al\(^{3+}\) on the surface. (a) PL emission spectra of solution containing the residual Al\(^{3+}\) as indicated (corresponding to the residual amount of Al\(^{3+}\) on the deprotected BP/Al\(^{3+}\)/BDT surface). Variation of UV-vis adsorption of BP (red column) and PO\(_4\)^{3-} (black column), measured with deprotected BP/Al\(^{3+}\)/BDT solution containing of (b\(_1\)) 0\%, (b\(_2\)) 25\%, (b\(_3\)) 50\%, (b\(_4\)) 75\%, and (b\(_5\)) 100\% of residual Al\(^{3+}\) on the surface (100\%, 75\%, 50\%, 25\%, and 0\% of residual Al\(^{3+}\) on the BP/Al\(^{3+}\)/BDT surface were achieved by immersing BP/Al\(^{3+}\)/BDT in 5 mmol/L EDTA-4Na solution for 0, 5, 10, 15, and 20 min, respectively). (c,d) TEM characterization of deprotected BP/Al\(^{3+}\)/BDT with different amount of residual Al\(^{3+}\) on the surface. TEM images of (c\(_1\)) 0\%, (c\(_2\)) 25\%, (c\(_3\)) 50\%, (c\(_4\)) 75\%, and (c\(_5\)) 100\% of the residual Al\(^{3+}\) on the BP/Al\(^{3+}\)/BDT surface after incubation in aqueous solution for 0 days. TEM images of (d\(_1\)) 0\%, (d\(_2\)) 25\%, (d\(_3\)) 50\%, (d\(_4\)) 75\%, and (d\(_5\)) 100\% of the residual Al\(^{3+}\) on the BP/Al\(^{3+}\)/BDT surface after incubation in aqueous solution for 7 days, 12 days, 30 days, 45 days, and 60 days, respectively.
Supplementary Note 4. Deprotection of other metal ion-stabilized BP complex

The strategy for regulating the BP reactivity can be extended to other metal ions, such as lanthanide metal ions (Fig. S9a), transition metal Fe$^{3+}$ ions (Fig. S9b), and Zn$^{2+}$ ions (Fig. S9c).

FTIR spectra prove that lanthanide metal ions can bind with BP. BDT can assemble on surface of BP/lanthanide metal ions complex. After treatment with EDTA-4Na, lanthanide metal ions together with BDT layer can be completely removed from the surface of BP.

For metal ions with strong electron-withdrawing ability, typically Fe$^{3+}$ (the electronic configuration of Fe$^{3+}$ is 3d$^5$4s$^0$, and the half-filled 3d orbitals endow Fe$^{3+}$ with high positive charge density) to promote the degradation of BP (50). Thus, directly binding BP with Fe$^{3+}$ resulted in fast degradation of BP. We slightly modified our protective strategy. Fe$^{3+}$ ions firstly bind with BDT to decrease the electron-withdrawing ability. The obtained Fe$^{3+}$/BDT could further bind to the surface of BP to form BP/Fe$^{3+}$/BDT. In addition, XPS analysis is carried out to analyze the surface compositions and chemical states of the elements present in BP/Fe$^{3+}$/BDT. Full-scan XPS spectra (Fig. S9b3) demonstrate the presence of the relevant elements (C, N, O, P, Fe, and S). In Fig. S9b4, the P 2p$_{3/2}$ and P 2p$_{1/2}$ doublet appear at higher binding energy (129.9 and 130.9 eV) relative to pure BP (129.6 and 130.7 eV). Such results verify that electron density shifting occurs from BP to Fe$^{3+}$/BDT. The high-resolution Fe 2p electron core-level XPS spectra of BP/Fe$^{3+}$/BDT is further investigated in Fig. S9b5. The two main peaks observed from BP/Fe$^{3+}$/BDT at the binding energy position of 712.3 and 726.1 eV correspond to the Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ respectively, confirming the existence of Fe$^{3+}$ (51). The high intensity of 2P$_{3/2}$ and 2P$_{1/2}$ in the XPS spectra of BP/Fe$^{3+}$/BDT suggests the low oxidation of BP within the composite. Upon treatment with EDTA-4Na, BP/Fe$^{3+}$/BDT can be deprotected.
Fig. S9. Characterization for the deprotected of BP/metal ion/BDT complex. (a) FTIR characterization of lanthanide metal ions protected BP and deprotected BP complex. (a1) FTIR spectra of BP, BP/La^{3+}/BDT, deprotected BP/La^{3+}/BDT and BDT. (a2) FTIR spectra of BP, BP/Sm^{3+}/BDT, deprotected BP/Sm^{3+}/BDT and BDT. (a3) FTIR spectra of BP, BP/Ho^{3+}/BDT, deprotected BP/Ho^{3+}/BDT and BDT. (b) Characterization of BP/Fe^{3+}/BDT and deprotected BP/Fe^{3+}/BDT. (b1) FTIR spectra of BP, BP/Fe^{3+}/BDT, deprotected BP/Fe^{3+}/BDT and BDT. (b2) Zeta potentials of BP, BP/Fe^{3+}/BDT and deprotected BP/Fe^{3+}/BDT. XPS spectra of BP/Fe^{3+}/BDT:
(b$_3$) full XPS, (b$_4$) HR-XPS spectra of P2p, and (b$_5$) HR-XPS spectra of Fe2p. (c) Characterization of BP/Zn$^{2+}$/BDT and deprotected BP/Zn$^{2+}$/BDT. (c$_1$) FTIR spectra of BP, BP/Zn$^{2+}$/NBT, deprotected BP/Zn$^{2+}$/NBT and NBT (NBT with a -NO$_2$ group (electron-withdrawing group) empowers Zn$^{2+}$/NBT stronger electron-withdrawing ability). (c$_2$) Zeta potentials of BP, BP/Zn$^{2+}$/NBT and deprotected BP/Zn$^{2+}$/BDT.
Fig. S10. Application of BP, BP/Al$^{3+}$/BDT and deprotected BP/Al$^{3+}$/BDT for solar vapor generation. (a) Schematic diagram of the solar vapor generation design where the PVDF is used to load BP/Al$^{3+}$/BDT. (b) Photograph of the PVDF film. (c) Surface temperature distribution of the four samples (PVDF film, BP/PVDF film, BP/Al$^{3+}$/BDT/PVDF film, deprotected BP/Al$^{3+}$/BDT/PVDF film) measured using a thermal image after 5 min solar illumination of 1 sun. (d) Evaporation water weights against time with the four samples (PVDF film, BP/PVDF film, BP/Al$^{3+}$/BDT/PVDF film, deprotected BP/Al$^{3+}$/BDT/PVDF film) under solar illumination of 1 sun. (e) Evaporation cycle performance of the four samples (PVDF film, BP/PVDF film, BP/Al$^{3+}$/BDT/PVDF film, deprotected BP/Al$^{3+}$/BDT/PVDF film) under solar illumination of 1 sun. (f) Photograph of initial three films (BP/PVDF film, BP/Al$^{3+}$/BDT/PVDF film, deprotected BP/Al$^{3+}$/BDT/PVDF film) and photograph of three films after 5 cycles. (g) Initial content of BP in three films (BP/PVDF film, BP/Al$^{3+}$/BDT/PVDF film, deprotected BP/Al$^{3+}$/BDT/PVDF film) and the content of BP in three films after 5 cycles, respectively. Photo Credit: Xiao Liu, Xiamen University.
**Table S1.** Comparison of stability for modified BP with different strategies.

| Stabilizer                                           | Modification       | Time monitored | Ref.                     |
|------------------------------------------------------|--------------------|----------------|--------------------------|
| AlO$_X$                                              | Surface capping    | 30 days        | *Nano Lett.* (52)        |
| Poly(lactic-**co**-glycolic acid)                    | Surface capping    | 8 days         | *Nat. Commun.* (53)     |
| *N*-Cyclohexyl 2-pyrrolidone                         | Surface capping    | 16 days        | *Nat. Commun.* (54)     |
| 7,7,8,8-Tetracyano-**p**-quinodimethane              | Noncovalent        | 2 days         | *Angew. Chem. Int. Ed.* (55) |
| Ionic liquid ([bmim][BF$_4$])                        | Noncovalent        | 90 days        | *Adv. Mater.* (56)      |
| Anthraquinone                                        | Noncovalent        | 30 days        | *ACS Nano* (19)          |
| Titanium sulfonate ligand (TiL$_4$)                  | Coordination       | 3 days         | *Angew. Chem. Int. Ed.* (17) |
| Ag$^+$                                               | Noncovalent        | 5 days         | *Adv. Mater.* (57)      |
| 4-Nitrobenzene-diazonium                             | Covalent           | 10 days        | *Nat. Chem.* (18)       |
| 4-Azidobenzoic acid                                 | Covalent           | 21 days        | *Angew. Chem. Int. Ed.* (58) |
| Al$_3^+$/BDT                                         | Coordination +     | 1 year         | This work                |
|                                                      | Surface capping    |                |                          |
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