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# Designs, Synthesis, Characterization and Direct Electrochemistry of Zinc-Porphyrin Bearing Pyrene Noncovalent Functionalized Graphene Oxide Sheet

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We have designed and synthesis a new compound of zinc-porphyrin bearing four pyrene groups (ZnP-t-P(py)$_4$) and prepared a new hybrid materials of ZnP-t-P(py)$_4$ with graphene oxide (GO) via non-covalent interactions. The ZnP-t-P(py)$_4$, along with four pendant pyrene entities ZnP-t-P(py)$_4$, stacking on the (GO) surface due to π-π interactions, has been revealed by AFM measurements. FTIR, UV-vis absorption confirm the non-covalent functionalization of the GO. Raman spectral measurements revealed the electronic structure of the GO to be intact upon hybrid formation. In this donor-acceptor nanohybrid, the fluorescence of photoexcited ZnP-t-P(py)$_4$ is effectively quenched by a possible electron-transfer process. The fluorescence and photoelectrical response measurements also showed that this hybrid may act as an efficient photoelectric conversion material for optoelectronic applications.

**Keywords** zinc-porphyrin, graphene oxide, non-covalent interaction, optoelectronic character

## Introduction

Recently, a lot of research effort has been devoted to understanding the physicochemical properties of the carbon allotrope-graphene with an atomically thin, 2D structure that consists of sp$^2$-hybridized carbons, and exhibits remarkable electronic and mechanical properties.[1-4] Theoretically, the molecules of other allotropic carbon forms can be built from graphene.[5a] For example it can be stacked to form 3D graphite, rolled to form 1D nanotubes, and wrapped to form 0D fullerenes. Usually, graphene oxide (GO) can be easily deposited on different substrates to produce continuous films for the construction of transparent conductors,[5b] photovoltaic devices,[6-8] and biosensors,[9-11] and hydroxyl groups at the basal planes of GO sheets, which is responsible for the formation of stable aqueous dispersions of GO.[12]

A number of types of covalently functionalized GO have been prepared by utilizing the above functional groups.[13,14] Such modified GO can be also applied as electron-accepting material in organic solar cells due to its unique structure and excellent electronic properties.[15] The interesting aspect attracting us is the non-covalent functionalization of GO, with planar organic molecules via π-π stacking, van der Waals, and/or electrostatic forces. More importantly, this easy method can endow GO with designed optoelectronic properties when it is combined with planar aromatic molecules such as porphyrins and phthalocyanines. To accomplish this, the donor, zinc porphyrin, has been functionalized with four pendant pyrene entities (Scheme 1, ZnP-t-P(py)$_4$)).[19] Due to the presence of four interacting pyrene entities on the GO' surface, stable ZnP-t-P(py)$_4$/GO hybrids are expected to form. As demonstrated here, this is indeed the case; additionally, the newly formed ZnP-t-P(py)$_4$/GO hybrids have allowed us to investigate the photoinduced electron transfer and photoelectrochemical responses of these ZnP-t-P(py)$_4$/GO nanohybrids have been tested.

## Experimental

### General conditions

NMR spectra were recorded on Bruker (300 MHz for $^1$H) instruments in DMSO-$d_6$ or $CDCl_3$ (TMS as an internal standard) solutions. Mass spectroscopy was recorded with autoflex TOF/TOF-(Bruker) and High Resolution Mass Spectra (LTQ-Orbitrap XL, Thermofisher). Analytical thin-layer chromatography (TLC) used $GF_{254}$. Flash chromatography was performed on silica gel (200—400 mesh). The morphologies of the modified surfaces were studied using atomic force microscopy (Agilent 5500 model, USA) in tapping mode.

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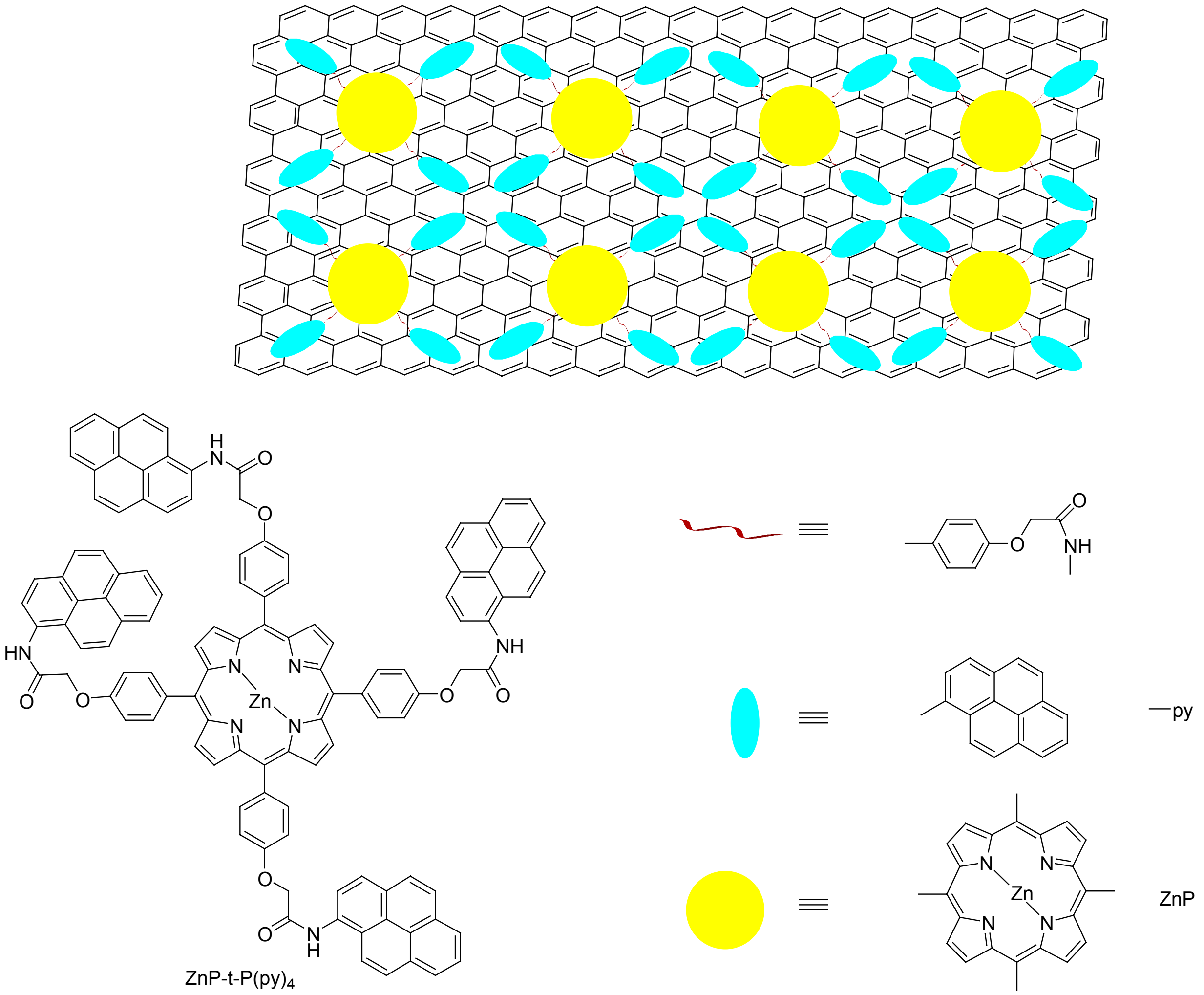
**Scheme 1** Schematic representation of the ZnP-t-P(py)$_4$ functionalized with four pendant pyrene entities on graphene oxide(GO)



IR data were measured on a KBr crystal plate, using a Bruker VECTOR 22 spectrophotometer. Resonance Raman spectra were recorded using a Renishaw-in via Raman spectroscopy (Renishaw, United Kingdom). UV/Vis absorption spectra were recorded using a Lambda 35 UV/Vis spectrometer (Perkin-Elmer instruments, USA). Fluorescence spectra were recorded at room temperature using an F900 fluorescence spectrometer (Edinburgh Instruments Ltd., United Kingdom). Photoelectrical response measurement experiments were performed using a CHI 660D electrochemical workstation (CH Instruments Inc., USA). All experiments were carried out at room temperature using a conventional three-electrode system with an indium-tin oxide (ITO) electrode as a working electrode, a platinum wire as an auxiliary electrode, saturated calomel electrode as a reference electrode, and supporting electrolyte is the solution of 0.1 mol/L ascorbic acid (AA) in 0.1 mol/L phosphate buffer solution (PBS, 200 mL mixture solvent composed by 0.5928 g $NaH_2PO_4$ and 5.8019 g $Na_2HPO_4$, pH=7.4).

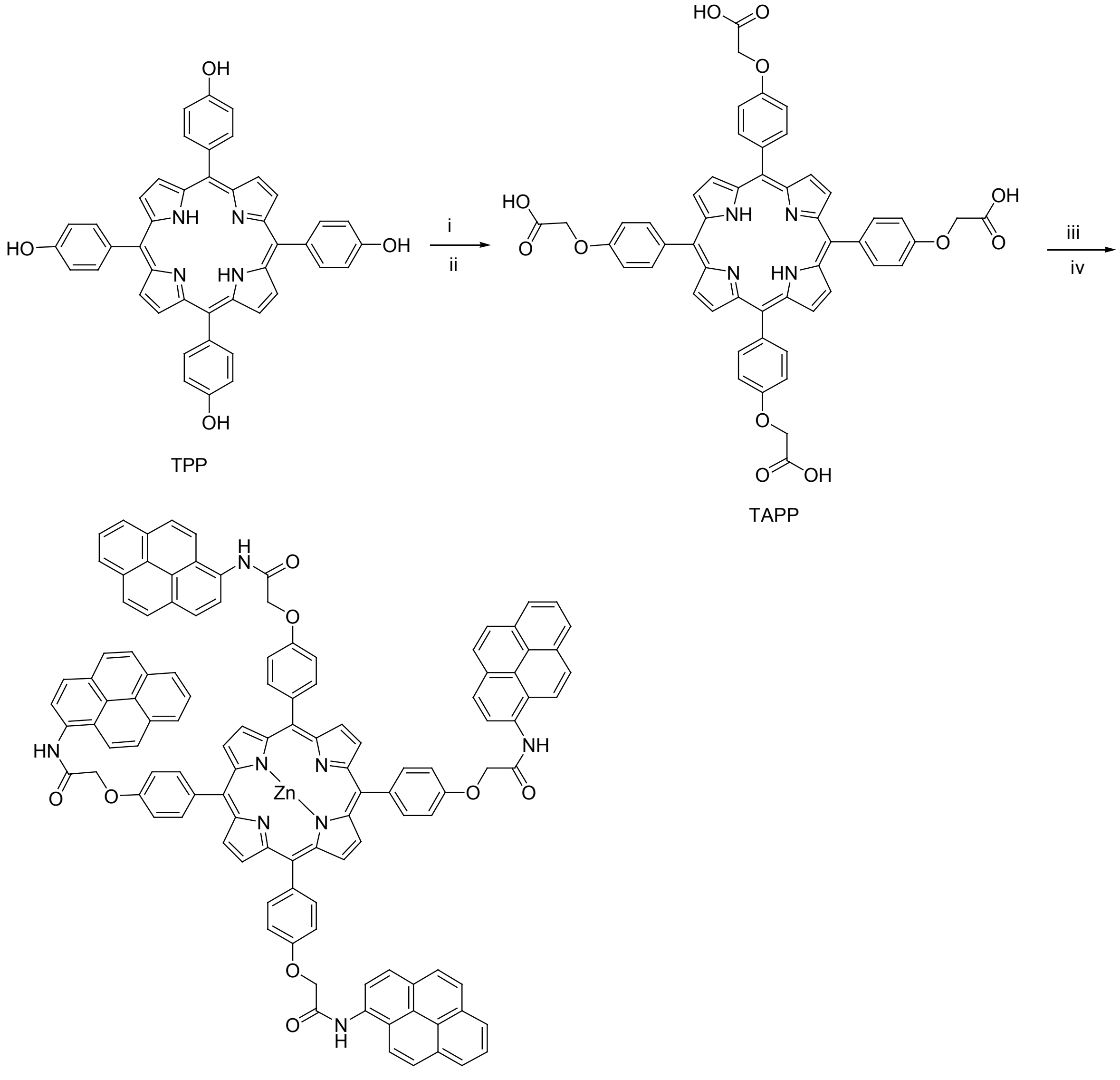
### Synthesis of graphite oxide (GO)

GO was produced by the modification of Hummers method[16-18] through the acid oxidation of flake graphite as originally presented by Kovtyukhova *et al.*[19,20]

### Synthesis of 5,10,15,20-tetra-4-oxy(acetic acid) phenylporphyrin (TAPP)

To a solution of 5,10,15,20-tetra-4-hydroxy-phenyl-Porphyrin (TPP)[21] (70 mg, 0.01 mmol) and ethyl bromoacetate (100 mg, 0.06) in 20 mL dry acetone was added $K_2CO_3$ (110 mg, 0.08 mmol). The mixture was heated under reflux for 24 h. After cooling to room temperature, the solvent and excess ethyl bromoacetate was removed via rotary evaporator. The solid was washed with methanol-water mixture (1 ∶ 1, *V* ∶ *V*).[22,23] The solid and KOH (56 mg) were dissolved in THF (20 mL), stirred and refluxed for 4 h. After cooling, 10% HCl was added into the solvent to neutralize excess KOH to pH=7, then removed the solvent and washed the residue with water. The crude product was recrystallized with methanol and water. Yield obtained was 90% (88 mg). $^1$H NMR (DMSO-$d_6$) $\delta$: 13.17 (s, 4H), 8.84 (s, 8H), 8.13 (d, $J$=8.11 Hz, 4H), 8.11 (d, $J$=8.11 Hz, 4H), 7.36 (d, $J$=7.84, 4H), 7.34 (d, $J$=7.84, 4H), 4.97 (s, 8H), −2.92 (s, 2H), autoflexTOF/TOF: $m/z$=910.73.

**Scheme 2** The synthesis of ZnP-t-P(py)$_4$: (i) ethyl bromoacetate, $K_2CO_3$, dry acetone refluxed for 24 h; (ii) KOH, THF, refluxed for 4 h; (iii) *N*-methylmorphine, ethylchloroformate, 1-aminopyrene, stirred at −12 ℃ for 2 h, then stirred at room temperature for 24 h; (iv) zinc acetate, DMF, refluxed for 3 h



ZnP-t-P(py)$_4$

## Synthesis of ZnP-t-P(py)$_4$

TAPP (90 mg, 0.1 mmol) was dissolved in dry THF (30 mL), stirred for 30 min. Then *N*-methyl morphine (54 mg, 0.52 mmol) was added to the solution, stirred for 40 min at −12 ℃ followed by the addition of ethylchloroformate (56 mg, 0.52 mmol). The mixture was stirred for 30 min at −12 ℃. 1-Aminopyrene (110 mg, 0.5 mmol) was added to the stirred solution and the mixture solution was stirred for 24 h during which the temperature was allowed to come to room temperature. After completion of reaction the solution was filtered and respectively washed with methol (50 mL), dichloromethane (50 mL). The residue was recrystallized with DMF.[24] Then zinc acetate was added to the DMF solvent of the $H_2P$-t-P(py)$_4$, stirred and refluxed for 3 h, filtered and washed with water. Yield obtained was 10% (18 mg); $^1H$ NMR ($CD_3CSCD_3$) $\delta$: 10.77 (s, 4H), 8.86 (s, 8H), 8.38—8.10 (m, 44H), 7.59 (d, $J$=7.58 Hz, 4H), 7.56 (d, $J$=7.58, 4H), 5.28 (s, 8H). The mass of the ZnP-t-P(py)$_4$ is 1770.3235, 1771.2788, 1773.0624 [ZnP-t-P(py)$_4$+$H^+$]; 1787.1266, 1789.1896 [ZnP-t-P(py)$_4$+$H^+$+$H_2O$].

## Preparation of ZnP-t-P(py)$_4$/GO and ZnP-t-P(py)$_4$/GO/ITO

2.0 mg sample of GO was added to 5.0 mg of ZnP-t-P(py)$_4$ dissolved in 20 mL of dry DMSO, and the reaction mixture was ultrasonic processed for 10 min and then stirred for 48 h at room temperature. The mixture was centrifugated for 20 min and the excess ZnP-t-P(py)$_4$ was washed by DMSO, followed by centrifugation at least three times, until the solution in the centrifuge tube turned colorless. At the end, 10 mL of fresh solvent was added to the resulting deposit and was sonicated for 15 min at 20 ℃. This homogeneous brown dispersion was stable for several days and used as mentioned in subsequent studies.[25]

The solution of 1 mg/mL ZnP-t-P(py)$_4$/GO was prepared for some subsequent measures. After the ITO electrode had been cleaned with isopropanol solution of 1.5 mol/L KOH, washed with acetone and twice-distilled water, and dried at room temperature, 20 μL suspension of ZnP-t-P(py)$_4$/GO was coated on the ITO electrode of 0.25 cm$^2$ and dried at room temperature to obtain ZnP-t-P(py)$_4$/GO/ITO.[28]

## Results and Discussion

### Characterization of the ZnP-t-P(py)$_4$/GO complex in solution

The presence of GO sheets in the suspension was confirmed by atomic force microscopy (AFM). The AFM image in Figure 1A shows a single GO sheet captured from the suspension on a mica substrate. The average thickness of GO was measured to be about 0.8 nm in water.[26] However, when GO was functionalized with ZnP-t-P(py)$_4$, the average thickness of a ZnP-t-P(py)$_4$/GO sheet was determined to be about 2.0 nm (Figure 1B), we assume that monolayered ZnP-t-P(py)$_4$-molecules covered both sides of graphene oxide sheet with offset face-to-face orientation via π-π interactions, by considering that the thickness of one porphyrin molecule is about 0.5 nm.[27,28]

### Raman spectrum

The samples were also characterized using laser Raman spectroscopy to obtain spectroscopic insight into the electronic structure of the GO in the ZnP-t-P(py)$_4$/GO nanohybrids. The Raman spectrum of GO (Figure 2) shows two prominent bands at about 1330 cm$^{-1}$ (D band originating from disorder-activated Raman mode) and 1576 cm$^{-1}$ (G band corresponding to sp$^2$ hybridized carbon).[29a,29b] In contrast to GO, the D and G bands of ZnP-t-P(py)$_4$/GO are shifted to the lower wavenumbers by $v$=11 and 15 cm$^{-1}$, respectively. It is worth pointing out that Raman spectroscopy could be used to determine the number of layers for $n$-layer graphene or graphene oxide by the shift and shape of the 2D peak, because the 2D peak in graphene is attributed to two phonons with opposite momentum in the highest optical branch.[29c] The 2D peak of ZnP-t-P(py)$_4$/GO appearing at 2709 cm$^{-1}$, shifts to the higher wavenumber value by 35 cm$^{-1}$ and becomes broader for an increasing number of ZnP-t-P(py)$_4$ layers with respect to single-layer graphene oxied (2D: 2674 cm$^{-1}$).[29a] The peak at 2924 cm$^{-1}$ (D+G mode) is attributed to defects, because it is a combination of two phonons with different momentum.[29d]

### FT-IR spectra

Figure 3 shows FT-IR spectra of ZnP-t-P(py)$_4$/GO, ZnP-t-P(py)$_4$, and GO. In the spectrum of ZnP-t-P(py)$_4$ and ZnP-t-P(py)$_4$/GO, the peak at 2919 cm$^{-1}$ corresponds to the sp$^3$ C—H characteristic stretching band. These results clearly indicate that the Zn-t-P(py)$_4$ molecules had been non-covalently bonded to the grapheme oxide by π-π stacking. The stretching band of C=O peak appeared at 1651 cm$^{-1}$, while the band of ZnP-t-P(py)$_4$/GO broadened because of including the group of —COOH (GO) and —CONH— (ZnP-t-P(py)$_4$).

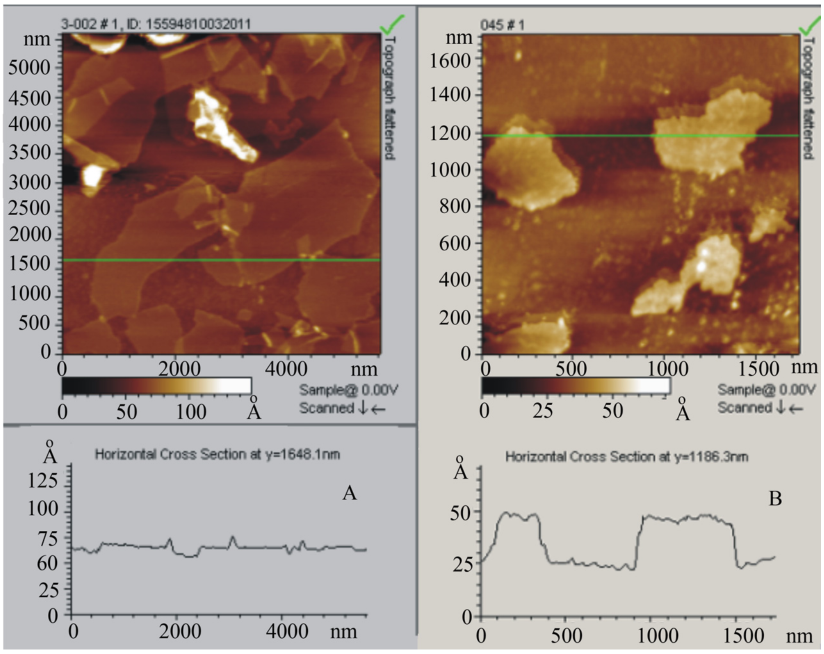


**Figure 1** Tapping-mode AFM images and cross-sectional analyses of (A) GO and (B) ZnP-t-P(py)$_4$/GO on mica.

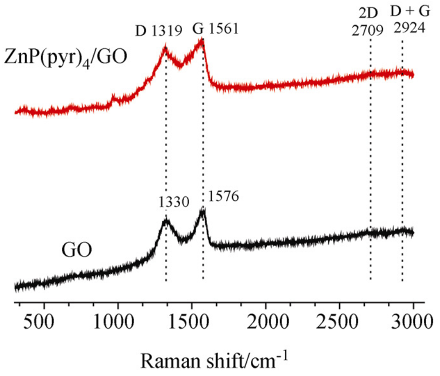


**Figure 2** The Raman spectra of GO (top), ZnP-t-P(py)$_4$/GO (bottom), $\lambda_{ex}=532$ nm.

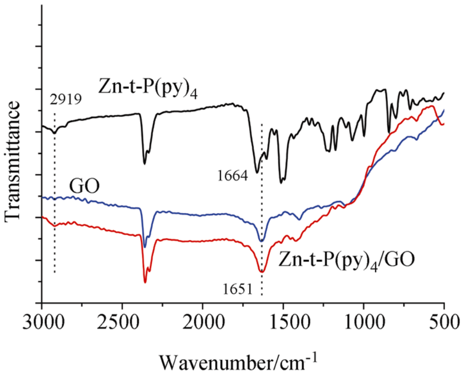


**Figure 3** FT-IR spectra of ZnP-t-P(py)$_4$, ZnP-t-P(py)$_4$/GO, and GO.

## UV/vis absorption

The UV/vis absorption spectra of ZnP-t-P(py)$_4$, and ZnP-t-P(py)$_4$/GO are shown in Figure 4. ZnP-t-P(py)$_4$ exhibited the typical Soret absorption at 431 nm and Q absorption at 561 and 602 nm. In the presence of GO, the Soret band of ZnP-t-P(py)$_4$/GO is redshifted from 431 to 433 nm, and the Q band is redshifted from 561 and 602 nm to 566 and 608 nm, which indicates the formation of a J-type aggregate nucleated on GO through π-π noncovalent interactions.[30]

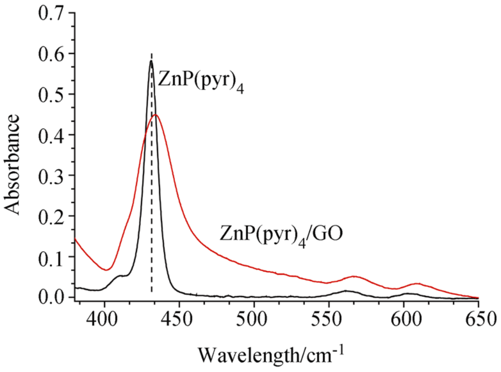


**Figure 4** UV/vis absorption spectra of ZnP-t-P(py)$_4$/GO and ZnP-t-P(py)$_4$ ($2\times10^{-6}$ mol/L) in DMSO.

## Steady-state fluorescence spectra

Figure 5 shows the steady-state fluorescence spectra of ZnP-t-P(py)$_4$ and ZnP-t-P(py)$_4$/GO hybrids, observed by the predominant excitation of the pyrene moiety (red line), exhibiting a main peak around 390, 409 and 434 nm in DMSO. A slight peak shift from 434—437 nm was observed for ZnP-t-P(py)$_4$/GO, supporting interaction between pyrene units and the GO surface. Under 350 nm excitation, some excited electrons of pyrene moiety return to ground state with transferring the energy to ZnP moiety (red line at 609 nm), because the ranges of pyrene emission cover the absorption wavelength of ZnP moiety,[31] then the excited state electrons of ZnP moiety transfer to GO surface. The ZnP moiety returns to steady-state (black line at 609 nm).[32] In the hybrids with GO, the Zn-porphyrin fluorescence intensity was found to be quenched over 80% of its original intensity around 610 nm.[5a,16]

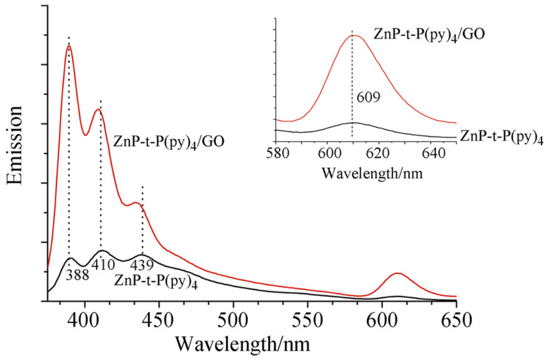


**Figure 5** Steady-state fluorescence spectra of ZnP-t-P(py)$_4$/GO and ZnP-t-P(py)$_4$ ($2\times10^{-6}$ mol/L) in DMSO, the inset is the Zn-porphyrin fluorescence intensity around 610 nm; $\lambda_{ex}=350$ nm.

## Photoelectrical response measurement

The typical photoelectrical response of the ZnP-t-P(py)$_4$/GO in thin film for the on/off light illumination cycles is shown in Figure 6. For the ZnP-t-P(py)$_4$/GO film on ITO substrate, a reversible rise/decay of the photocurrent in response to the on/off illumination step is observed. After light illumination, the photocurrent is about 134% higher than that before illumination and 65.5 times as blank experiment. Compared with reported literature[33c] which connected porphyrin and GO via covalent, this hybrid has higher photocurrent and lower dark current. In addition, the interaction between porphyrin and GO via noncovalent method is convenient to be prepared. Blank experiments carried out with ITO coated with GO films[33d] produced a negligibly small photoelectrochemical effect under similar experimental conditions. Moreover, it is evident that the photoelectrical response measured for the ZnP-t-P(py)$_4$/GO shows evident photocurrent stability when exposed to several on/off cycles. According to the results reported by others,[32] this phenomenon shows that there is electron transfer from ZnP-t-P(py)$_4$ to GO and higher

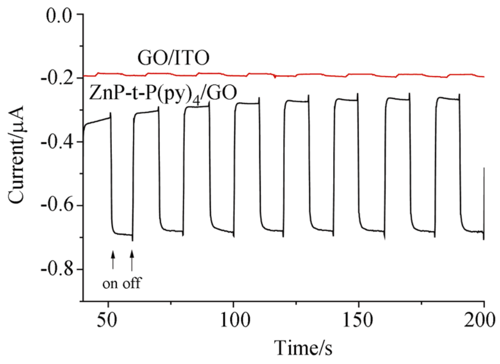
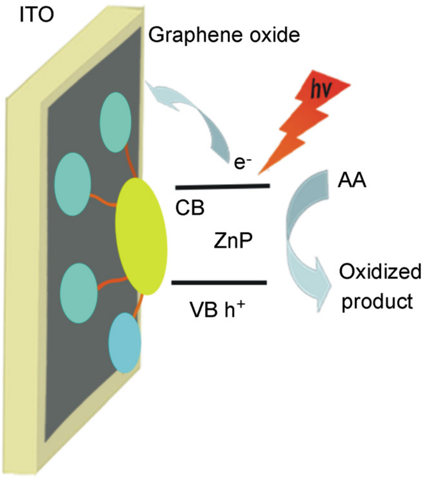


**Figure 6** The typical photoelectrical response of the ZnP-t-P(py)$_4$/GO film on ITO substrate under white light illumination at an applied potential of −0.4 V (solution: $H_2O$ of 0.1 mol/L AA and 0.1 mol/L PBS, pH=7.4).

photocurrent[16] under illumination. Thus, this hybrid can act as the photoelectric conversion material for optoelectronic applications.

The mechanism of photocurrent generation by ZnP-t-P(py)$_4$ was speculated using a mono-layer as a model (Scheme 3). When ZnP-t-P(py)$_4$ absorbs photons with energies higher than its band gap, electrons are excited from the (occupied) valence band to the (empty) conduction band, forming the electron-hole pairs. The electron transfers to the GO electrode and generates photocurrent because the energy level of the ZnP-t-P(py)$_4$ is higher than the conduction-band of GO.[34a] The injection of the conduction-band electrons into the electrode yields the photo-current, whereas the electron donor (ascorbic acid, AA) provides the electrons to the valence-band holes, thus complete the photo-current generation cycle.[34b]

**Scheme 3** Photocurrent generation mechanism of a graphene oxide and ZnP-t-P(py)$_4$ monolayer



## Conclusions

In summary, we have designed a new ZnP-t-P(py)$_4$/GO hybrid material via non-covalent interactions. The ZnP-t-P(py)$_4$, along with four pendant pyrene entities ZnP-t-P(py)$_4$, stacking on the GO surface due to π-π interactions, has been revealed by AFM measurements. FTIR, UV-vis absorption spectra confirm the non-covalent functionalization of the GO. Raman spectral measurements revealed the electronic structure of the GO to be intact upon hybrid formation. In this donor-acceptor nanohybrid, the fluorescence of photoexcited ZnP-t-P(py)$_4$ is effectively quenched by a possible electron-transfer process. Fluorescent and photoelectrical response measurements also reveal that this hybrid may act as an efficient photoelectric conversion material for optoelectronic applications.

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