The Hybrids of Graphene with the Polymer of Porphyrin: Synthesis, Characterization and Their Nonlinear Optical Properties

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Abstract. A series of comb-shaped porphyrin polymers were synthesized by RAFT polymerization which modified the graphene via π-π bond to synthesize the polymer composite and made the graphene could better disperse in organic solvents. The reverse saturable absorption (RSA) of the hybrid materials were studied. The π-π bonding between poly-porphyrin (PPor) and graphene was confirmed by UV-Vis and fluorescence spectra. The strong fluorescence quenching in composites suggested the energy transfer between the PPor and graphene. The RSA properties were studied by open aperture Z-scan technique at 532 nm in nanosecond regime. At same transmission intensity, the hybrids showed a better NLO property which compared to the PPor and graphene.

1. Introduction

In recent years, with the development of graphene, its stable conjugate structure made it had special properties which made them particularly attractive for use in many fields [1]. Therefore, the non-linear optical properties of phthalocyanine, porphyrin compounds and graphene hybrid materials had attracted attention [2-5]. However, due to the 18π-electron conjugated structure of porphyrin and phthalocyanine [6], porphyrin and phthalocyanine would appear certain aggregation phenomenon in the process of solution self-assembly, which leaded to the reduction of nonlinear optical performance of composite [7,8]. Herein, a series of comb-shaped porphyrin polymers were synthesized by Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) [9,10] which modified the graphene via π-π bond to synthesize the polymer composite. On the one hand, the well solubility of the polymer was used to improve the dispersibility of the composite material in the solution. On the other hand, porphyrin polymers were beneficial to prevent the occurrence of aggregation between porphyrin molecules, which resulted in the further increases of nonlinear optical performance.

2. Experimental Section

2.1. Materials

All materials for the experiment were purchased from Tokyo Chemical Industry Company. Tetrahydrofuran (THF) was distilled prior to use. Acetone, Propionic acid and 1,4-Dioxane were purchased from Beijing Chemical Co. Ltd.

2.2. Measurements

FTIR spectra were performed on a PE Frontier spectrometer. The UV-vis absorption spectra were recorded with a Shimadzu corporation UV-2600 spectrophotometer. Fluorescence spectra were
recorded with a Fluoro-Max-P fluorescence spectrophotometer. Gel permeation chromatograph (GPC) was conducted on Waters e2695. The nonlinear absorption properties of all samples were measured with linearly polarized 7 ns pulsed 532 nm light generated from a mode-locked Nd:YAG laser with a repetition rate of 10 Hz.

2.3. Synthesis of TPP-OH
TPP-OH was synthesized according to the reference.[11] Benzaldehyde (6.90 mL, 6.9 mmol), p-hydroxybenzaldehyde (3.05 g, 28 mmol) and pyrrole (4.67 mL, 6.7 mmol) were dissolved in propionic acid (80 mL) and heated to 140 °C for 2 h. After cooling to 60 °C, ethanol (60 mL) was dropped to the mixture, the solution was stored for 12 h, and then the reaction mixture was subjected to suction filtration and washed with ethanol to remove pyrrole aggregates. The mixture was purified by silica gel chromatography using the DCM as eluent to afford TPP-OH as a purple powder. Yield: 700 mg (8%). 1H NMR (500 MHz, CDCl3), δ (ppm): 8.90 (m, 8H), 8.17 (m, 6H), 8.12 (m, 2H), 7.20 (m, 9H), 7.18 (m, 2H), -2.66 (s, 2H).

2.4. Synthesis of TPPC6-OH
TPPC6-OH was synthesized according to the reference.[12] TPP-OH (0.2 g, 0.32 mmol), 6-chloro-1-hexanol (0.05 mL, 0.32 mmol) and potassium hydroxide (0.003 g, 0.04 mmol) were dissolved in anhydrous acetonitrile (100 mL) at 90 °C and stirring for 24 h. The mixture was cooled down to 25 °C, the mixture was washed by the saturated Na2CO3, the organic solution was removed by vacuum distillation. The mixture was purified by silica gel chromatography using the DCM as eluent to afford TPP-OH as a purple powder. Yield: 0.19 g (73.6%). 1H NMR (500 MHz, CDCl3), δ (ppm): 8.92 (m, 8H), 8.27-8.15 (m, 8H), 7.82 (m, 9H), 7.33 (m, 2H), 4.30 (t, 2H), 3.83 (t, 2H), 2.09 (m, 2H), 1.80-1.65 (m, 6H), -2.53 (s, 2H).

2.5. Synthesis of TPPC6MA
TPPC6MA was synthesized according to the reference.[13] To a solution of TPPC6-OH (0.1 g, 0.5 mmol) and triethylamine (0.06 g, 0.14 mmol) in anhydrous dichloromethane (30 mL) in an ice bath (0 °C), methacryloyl chloride (0.1 g, 0.97 mmol) in 5 mL anhydrous DCM was dropwise added and stirring at 25 °C for 12 h. The reaction mixture was diluted with dichloromethane and then extracted saturated Na2CO3, the organic solution was removed by vacuum distillation. The mixture was purified by silica gel chromatography using the DCM as eluent to afford TPPC6MA as a purple powder. 1H NMR (500 MHz, CDCl3): δ (ppm): 8.87 (m, 8H), 8.21 (m, 6H), 8.11 (m, 2H), 7.76 (m, 9H), 7.28 (m, 2H), 6.15 (s, 1H), 5.59 (s, 1H), 4.26 (m, 4H), 2.01 (m, 2H), 1.99 (s, 3H), 1.84-1.61 (m, 6H), -2.77 (s, 2H).

2.6. Synthesis of PTPPC6MA(PPor)
Under nitrogen atmosphere, TPPC6MA (0.2 g, 0.25 mmol), AIBN (0.01 mg, 0.06 mmol) and Chain transfer agent (0.025 mg, 0.08 mmol) were dissolved in 1,4-dioxane (1 mL) and heated to 65 °C. After 24 h, the reaction was quenched by exposure to air. The polymer product was purified by precipitation in excess cold methanol, after which the product was lyophilized to give PTPPC6MA as a red solid. Yield 0.1 g (63.2%). Mn, GPC: 2700 g mol⁻¹; Mw/Mn = 1.12.

2.7. Synthesis of PPor/G
PPor (30.5 mg, 0.01 mmol) and graphene (100 mg) was distributed in anhydrous DMF (10 mL) and stirring at 25 °C for 24 h. The hybrid product was purified by precipitation in water and dried under vacuum to afford PPor/G as a purple powder.

3. Results and Discussion

3.1. Synthesis of PPor
To identify the construct of the as-prepared materials, the synthesized products are characterized by
$^1$H NMR, GPC, and FTIR spectra. The successful preparation of polymers was confirmed by FTIR and $^1$H NMR (Figure 1 and 2). The molecular weight and PDI were obtained by GPC (Figure 3).

The detailed results of the successful synthesis of PPor$_{1,3}$ are summarized in Table 1, which indicated that the $M_n$ of PPor was increased with the increment of the mole ratio and the narrow $M_w/M_n$ exhibited the characteristic of a controlled/living polymerization. Moreover, due to the existing of a small part of deactivated initiator, which resulted the value of $M_n$, $M_w$ was higher than $M_n$ theo.

**Figure 1.** FTIR spectra of TPP-OH (a) TPPC6-OH (b) TPPC6MA (c) and PPor (d).

**Figure 2.** $^1$H NMR spectra of TPPC6-OH, TPPC6MA and PPor in CDCl$_3$.

**Figure 3.** GPC of PPor$_1$, PPor$_2$ and PPor$_3$.

**Table 1.** Characteristics of monomers and brush-shaped block copolymer, PPor$_1$, PPor$_2$ and PPor$_3$.

| Sample    | mole ratio | $M_n$, theo (g mol$^{-1}$) | $M_n$, GPC (g mol$^{-1}$) | $M_w$, GPC (g mol$^{-1}$) | $M_w/M_n$ (g mol$^{-1}$) | Conv. (%) |
|-----------|------------|----------------------------|---------------------------|---------------------------|--------------------------|-----------|
| PPor$_1$  | 1/3        | 2500                       | 2700                      | 2800                      | 1.06                     | 63.5      |
| PPor$_2$  | 1/5        | 4000                       | 4200                      | 4300                      | 1.03                     | 58.4      |
| PPor$_3$  | 1/7        | 5800                       | 7000                      | 7100                      | 1.01                     | 69.3      |

$^a M_n$, theo = $[MM]_0/[I]_0 \times$ molecular weight of monomers $\times$ conversion (%).

$^b$ Determined by GPC equipped with a RI detector in THF using PS standards.
3.2. Photophysical Properties of PPor/G
The dispersion characterization of PPor/G in organic solvents was determined by UV-vis spectra. The graphene shows a broad absorption band with decreasing intensity and stretching to 800 nm. For PPor, the results show one characteristic peak at 425 nm and 4 characteristic peaks located at around 500-700 nm which belong to the B-band and Q band of porphyrin, respectively (figure 4(A)). For PPor/GO, the B-band shifted to 417 nm, which suggests that the ground-state electronic interactions between the porphyrin and graphene. As presented in figure 4(B). The complex of polymer and graphene significantly improves the dispersability of polymer composite, indicating the hybrid could dispersed in organic solvents.

**Figure 4.** (A)UV-vis spectra of PPor, PPor/G, Graphene in DMF. (B) Shown in the inset is the plots of absorbance at 422 nm versus concentration.

**Figure 5.** Fluorescence spectra of pure porphyrins and their graphene adducts: PPor$_1$ and PPor$_1$/GO [$\lambda_{ex}=360$ nm]; PPor$_2$ and PPor$_2$/GO [$\lambda_{ex} = 360$ nm]; PPor$_3$ and PPor$_3$/GO [$\lambda_{ex} =360$ nm].

Fluorescence spectra further supports the successful preparation of all the products. The PPor$_{1,3}$'s fluorescent emissions were show in figure 5, the fluorescence intensity of PPor was increased with the increment of the mole ratio. However, the fluorescence intensity of PPor$_{1,3}$/G exhibit significantly reduced in the 625-700 nm region. As a result, the fluorescence intensity was quenched by 98.88%/98.53%/98.48% in PPor$_1$/G, PPor$_2$/G and PPor$_3$/G, respectively, which indicate the successful preparation of composite materials and effective energy transfer.

3.3. Reverse Saturable Absorption Properties of PPor/G
To research the effect of molecular weight on reverse saturable absorption performance ($Im \chi^{(3)}$) of
PPor/G, the Z-scan spectroscopy was carried out and the results were showed in table 2. As the molecular weight increasing, the RSA of PPor exhibit a decreasing trend, however, the performance of RSA is significantly improved while compounded with graphene and the RSA performance was decreased with the increment of the molecular weight, which belong to the energy transfer between the different component in the composite. Due to the flexible groups of polymers create the steric hindrance which hinders the π-π adsorption between graphene and porphyrin, leading to the decreased energy transfer between the porphyrin and graphene. Resulting to the RSA performance of PPor/G decreased with the increment of the molecular weight.

| Sample  | Linear transmittance | β (m W⁻¹) | Im(β) (esu) |
|---------|----------------------|-----------|-------------|
| PPor₁   | 69%                  | 4×10⁻¹⁰   | 1.31×10⁻¹¹  |
| PPor₂   | 71%                  | 3.3×10⁻¹⁰ | 1.08×10⁻¹¹  |
| PPor₃   | 70%                  | 2.3×10⁻¹⁰ | 7.56×10⁻¹²  |
| PPor₁/G | 68%                  | 4×10⁻⁹    | 1.3×10⁻¹⁰   |
| PPor₂/G | 70%                  | 5.5×10⁻¹⁰ | 1.8×10⁻¹¹   |
| PPor₃/G | 67%                  | 2.4×10⁻¹⁰ | 7.7×10⁻¹²   |

4. Conclusion
A comb-type porphyrin polymer with TPPC6MA as a monomer was prepared by RAFT and compounded with graphene to prepare the polymer composite. The structure of products was affirmed by FT-IR, ¹H NMR and GPC. The low polydispersity index indicates that the reaction could be well controlled. UV-Vis and fluorescent indicated the success of the complex, which proved the existence of energy transfer between PPor and graphene. However, the RSA performance of PPor/G showed a decreasing trend with the molecular weight increased.

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