Porphyrin and Fullerene Covalently Functionalized Graphene Hybrid Materials with Large Nonlinear Optical Properties

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Contents

1. Synthesis

Synthesis of Graphene-TPP: The synthesis of Graphene-TPP is shown in Scheme 1. TTP-NH$_2$ was synthesized according to the literature.[1] Graphene oxide (30 mg) was prepared using our modified Hummers method.[2] and it was then refluxed in SOCl$_2$ (20 ml) in the presence of DMF (0.5 ml) at 70 ^{o}C for 24 h under argon atmosphere. At the end of the reaction, excess SOCl$_2$ and solvent were removed by distillation. In the presence of triethylamine (Et$_3$N, 0.5 ml), the above product was allowed to react with TTP-NH$_2$ (30 mg) in DMF (10 ml) at 130 ^{o}C for 72 h under argon. After the reaction, the solution was cooled to room temperature, and then poured into aether (300 ml) to precipitate the product. The product was isolated by filtration on a Nylon membrane (0.22 μm). The excess TTP-NH$_2$ and other impurities were removed through 5 washing cycles that included sonication, filtration (discarding the filtrate), re-suspending the solid in THF (50 ml) each time. The precipitate was washed with CHCl$_3$ 5 times following the above procedure. UV and TLC were used to check the filtrate to ensure no TTP-NH$_2$ existed in the final washing. And then Graphene-TPP was washed with a small quantity of H$_2$O to remove Et$_3$N·HCl, and finally dried under vacuum to yield the hybrid Graphene-TPP.

Synthesis of Graphene-C$_{60}$: The synthesis of Graphene-C$_{60}$ is shown in Scheme 2. Pyrrolidine fullerene was prepared by a photochemical reaction between amine acid esters and C60 [3]. GO (50 mg) was reacted with SOCl$_2$ (20 ml) in the presence of N,N-dimethyl-formamide (DMF) (0.5 ml) at 70 ^{o}C for 24 h to abtain the acyl-chloride functionalized GO. The excess SOCl$_2$ was evacuated under reduced pressure, and washed with anhydrous toluene for three times to remove the residual SOCl$_2$. Then pyrrolidine fullerene (44 mg) and triethylamine (1 ml) in CHCl$_3$ (40 ml) were added to the above residue. The solution was purged with Ar and stirred for 3 days in dark at room temperature. On completion of the reaction, the solution was poured into acetone. The resultant suspension was collected on a polycarbonate membrane filter of 100 nm pore size and washed with CHCl$_3$ (sonication) for several times until the unreacted pyrrolidine fullerene was completely removed (monitored by thin layer

chromatography). The deposition was further washed with water and acetone, then dried under vacuum to yield Graphene-C_{60} hybrid (24 mg).

2. Instruments and measurements.

FTIR spectra were obtained with a BRUKER TENSOR 27 instrument. All IR samples were prepared as pellets using spectroscopic grade KBr. UV-Vis spectra were obtained with a JASCO V-570, and UV-Vis spectra were recorded on a VARIAN Cary 300 spectrophotometer using a quartz cell with a path length of 10 mm. Raman spectra were measured by a Renishaw inVia Raman microscope at room temperature with the 514 nm line of an Ar ion laser as an excitation source. Fluorescence spectra were obtained with a FluoroMax-P instrument. Transmission electron microscope (TEM) images were obtained on a JEM.2010FEF instrument operated at 200 kV. Sample preparation involved water bath sonicating (Gongyi Yuhua Instrument Co., LTD, Model: KQ400B, 400 W) materials in DMF for 2h and dropping the resulting suspension onto carbon-coated copper grids. H^1NMR spectra were recorded on a BRUKER (300 MHz) spectrometer using TMS as the internal standard. Tapping mode AFM measurements were performed using Multimode SPM from Digital Instruments with Nanoscope IIIa Controller and the samples for AFM images were prepared by depositing a dispersion of graphene oxide/H_2O solution (0.2 mg/ml) on a freshly cleaved mica surface. Graphite was obtained from Qingdao Huarun graphite Co. Column chromatography was performed with silica gel (100-200 mesh, Qingdao Haiyang Chemical Co., Ltd, China).
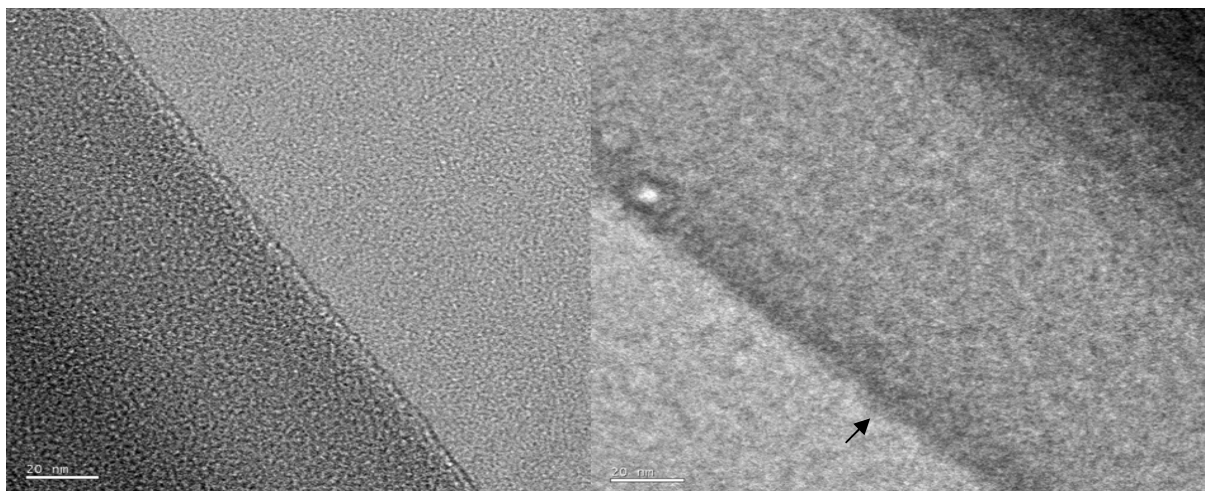
3. Microscopy and Spectroscopy.

Fig. S1. TEM images of graphene oxide (left) and Graphene-TPP (right). The edge of graphene oxide was significantly roughened by the coverage of soft material, indicating the presence of TTP-NH$_2$ attached to the graphene oxide edge.
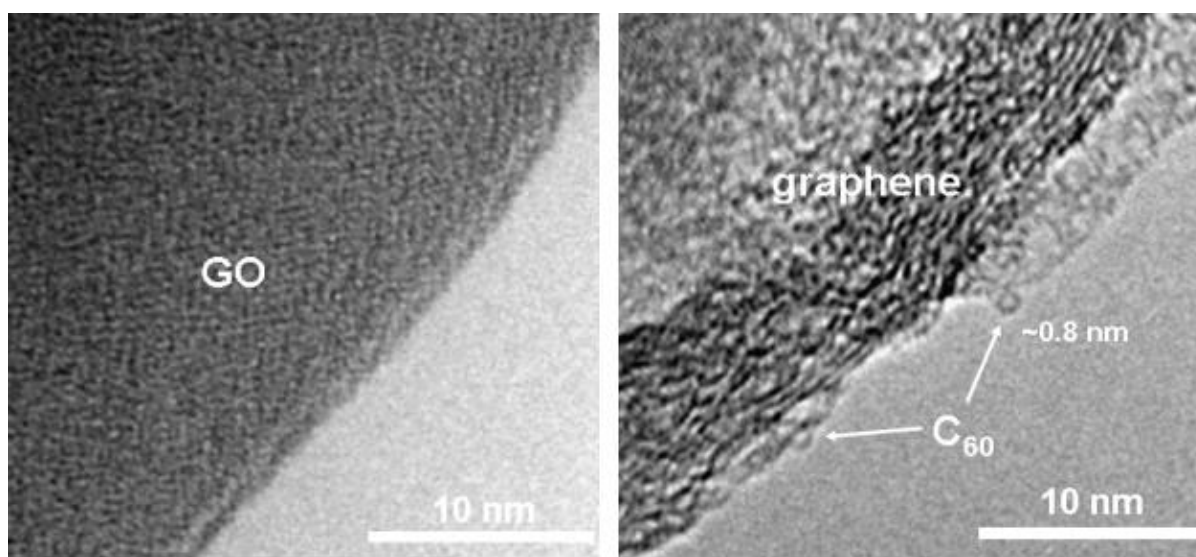

Fig. S2. TEM images of GO (left) and graphene–C60 hybrid (right). The images were acquired from samples deposited onto a holey carbon support film.
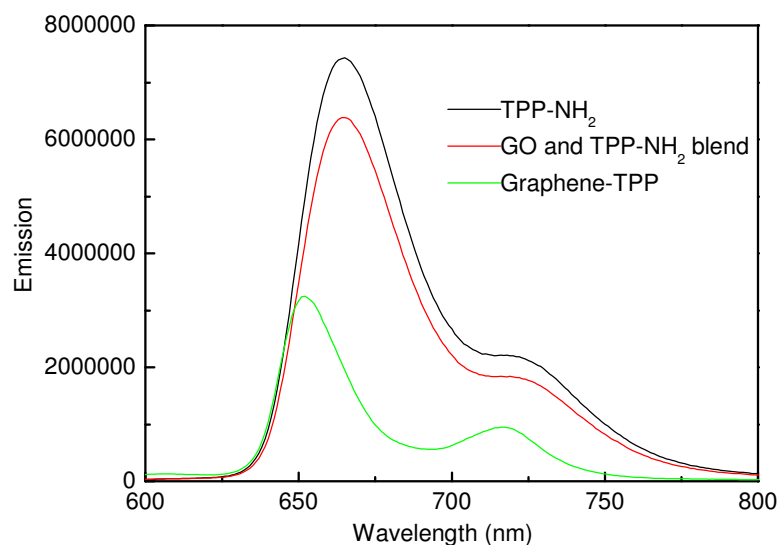
Fig. S3. Fluorescence spectral changes observed for TPP-NH$_2$, the controlled sample, Graphene-TPP in DMF with the normalization of the absorbance of the Soret band excitation wavelength (419 nm) to the same value (0.24). The observed luminescence quenching indicated that there was a strong interaction between the excited state of TPP and graphene moieties in the hybrid.
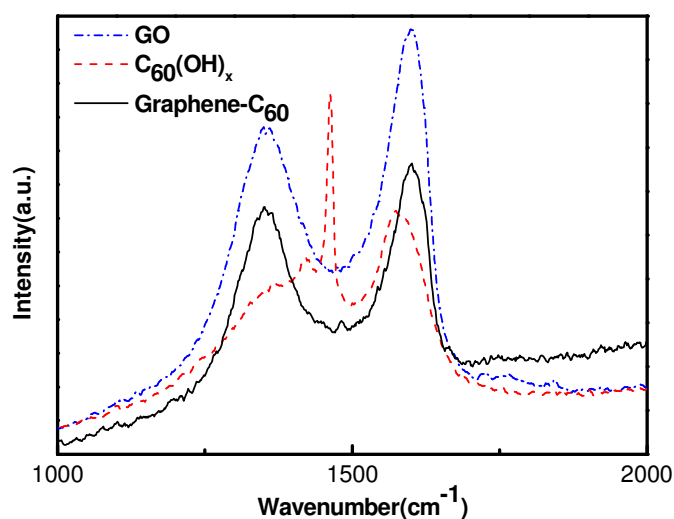

Fig. S4. Raman spectra of GO (dashed line), pyrrolidine fullerene (dotted line) and Graphene–C$_{60}$ (solid line) excited at 514 nm. The peak at 1482 cm^{-1} in the Graphene–C$_{60}$ is the Ag(2) mode of the C$_{60}$ cage, which is shifted by 13 cm^{-1} compared with that of the pyrrolidine–C$_{60}$. This relative shift sufficiently suggests a strong interaction between the C$_{60}$ cage and the graphene sheet.
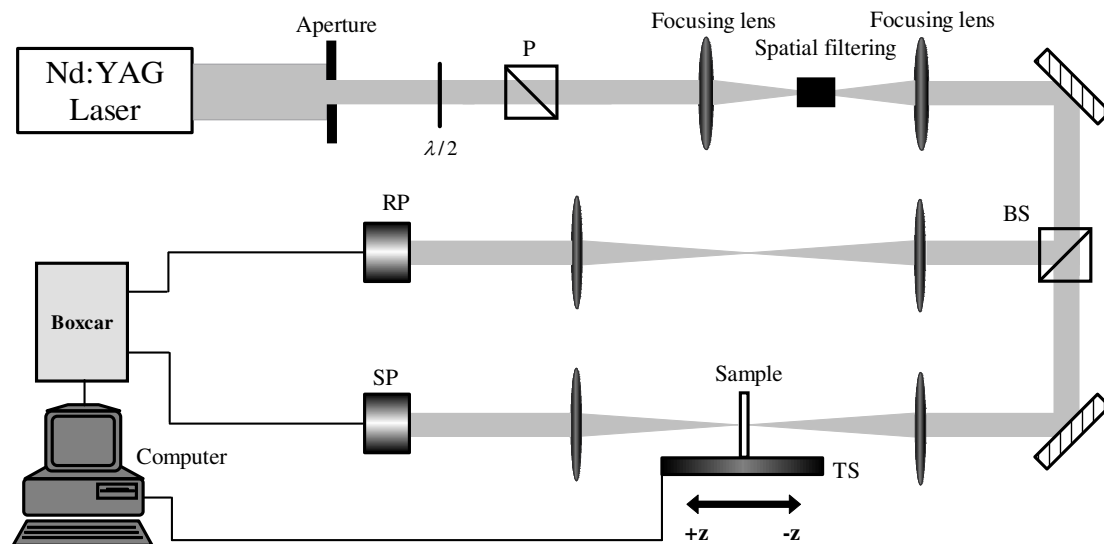
4. Nonlinear optical studies.

Fig. S5. Setup of Z-scan experiments. P = polarizer, BS = beam splitter, RP = reference detector, SP = signal detector.
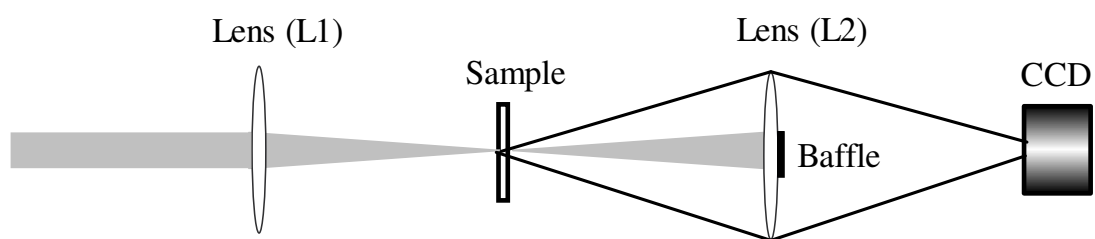

Fig. S6. Setup of the nonlinear scattering experiments.

5. Computations.

To compare quantitatively, we theoretically fitted the experimental results of open aperture Z-scan to obtain effective nonlinear absorption coefficients β.[4] Because the length L of the samples used in our experiments was longer than the Rayleigh length of beam z_0, a thick sample model and a numerical method were used to solve the propagation equation of the electric field envelope. The partial differential equation that describes the propagation of the electric field envelope E in a nonlinear medium can be written as:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial E}{\partial r}\right) - 2ik\frac{\partial E}{\partial z} - ik\alpha E + \frac{2k^2}{n_0}n_2|E|^2 \cdot E = 0 , \tag{1}$$

$$\alpha = \alpha_0 + \beta \cdot I , \tag{2}$$

where α_0 is linear absorption coefficient, n_2 is nonlinear refractive index, and k is wave vector. The numerical simulation of Eq. (1) was made by the Crank–Nicholson finite difference method.

Reference:

[1] W. J. Kruper, T. A. Chamberlin, M. Kochanny, J. Org. Chem. **1989**, 54, 2753.

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[3] Gan LB, Zhou DJ, Luo CP, Tan HS, Huang CH, Lu MJ, et al. J Org Chem 1996;61(6):1954–61.

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