Electronic Supplementary Information (ESI)

Functionalization of graphene by tetraphenylethylene using nitrene chemistry

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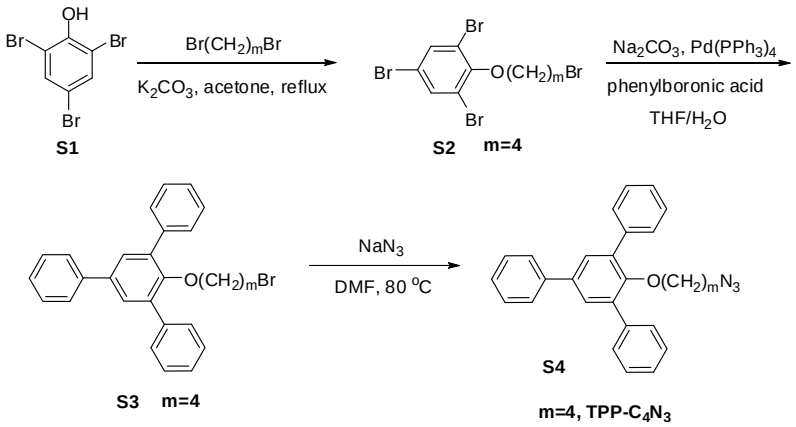
Experimental Section

Synthesis and Characterization



S1 **S2** **m=4** **S3** **m=4** **S4** **m=4, TPP-C_4N_3**

Synthesis of Compound S3

S1, **S2**, and **S3** were prepared according to our previous work[1] except 1,4-dibromobutane was used

instead of 1-bromobutane. A colorless oil was obtained in 96% (1.01g). ^{1}H NMR ($CDCl_3$, 300 MHz), δ(TMS, ppm): 7.66 (m, 6H, Ar-H), 7.56 (s, 2H, Ar-H), 7.47-7.34 (m, 9H, Ar-H), 3.24 (t, J = 11.4 Hz, 2H, -O-CH_2-), 3.00 (t, J = 13.5 Hz, 2H, -CH_2-Br), 1.52 (m, 2H, -CH_2-), 1.33 (m, 2H, -CH_2-).

Synthesis of Compound S4

The procedure was similar to that of **TPE-C_4N_3**. A white solid was obtained in 92% (852 mg). ^{1}H NMR ($CDCl_3$, 300 MHz), δ(TMS, ppm): 7.65 (m, 6H, Ar-H), 7.57 (s, 2H, Ar-H), 7.45-7.37 (m, 9H, Ar-H), 3.24 (t, 2H, -O-CH_2-), 2.87 (t, 2H, -CH_2-N_3), 1.24 (m, 4H, -CH_2-).

Synthesis of Compound PB-Cl

1-pyrenebutyric acid (577 mg, 2 mM), 2-chloroethanol (169 mg, 2.1 mM), dicyclohexylcarbodiimide (DCC) (825 mg, 4 mM), and 4-(N,N'-dimethyl)aminopyridine (DMAP) (73 mg, 0.6 mM) were dissolved in dry CH_2Cl_2 (50 mL) and stirred at room temperature for 24 h. The precipitate was filtered and the crude product was purified by column chromatography using chloroform/petroleum ether (1/5, v/v) to afford a yellow solid (652 mg, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz), δ(TMS, ppm): 8.29 (d, 1H, Ar-H), 8.18-8.11 (m, 4H, Ar-H), 8.04-7.97 (m, 3H, Ar-H), 7.88 (d, 1H, Ar-H), 4.35 (t, 2H, -O-CH_2-), 3.69 (t, J = 10.8 Hz, 2H, -CH_2-Cl-), 3.41 (t, J = 15 Hz, 2H, Ar-CH_2-), 2.52 (t, J = 14.1 Hz, 2H, -CH_2-CO-), 2.22 (m, 2H, -CH_2-).

Synthesis of Compound PB-N_3

The procedure was similar to that of **TPE-C_4N_3**. A yellow solid was obtained in 90% (530 mg).^{1}H NMR ($CDCl_3$, 300 MHz), δ(TMS, ppm): 8.32 (d, 1H, Ar-H), 8.18-8.11 (m, 4H, Ar-H), 8.04-7.97 (m, 3H, Ar-H), 7.87 (d, 1H, Ar-H), 4.25 (t, 2H, -O-CH_2-), 3.69 (t, 2H, -CH_2-N_3-), 3.45 (t, 2H, Ar-CH_2-), 2.52 (t, 2H, -CH_2-CO-), 2.17 (m, 2H, -CH_2-).

Syntheses of PB-G and TPP-C_4N_3-G.

The procedures were similar to that of **TPE-C_4N_3-G**.

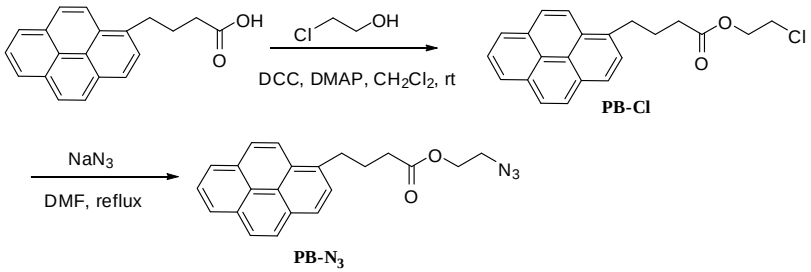


Figure S1. Synthetic routes to **PB-N_3**.

Figure S2. Photograph of the reaction system of **PB-G**, which was taken after one week.

Figure S3. Photographs of graphene (left) and **TPE-C_4N_3-G-In** (right) in THF, both of the samples were prepared by sonication for 5 seconds, and the photographs were taken after 30 min.

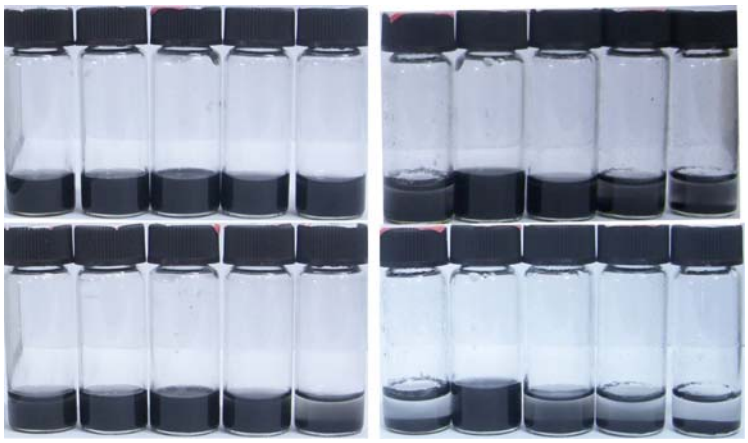


Figure S4. Dispersion stabilities of **TPE-C_4N_3-G-In** (left) and graphene (right) in toluene, DMF, $CHCl_3$, ethanol and acetone (from left to right) without sonication. The samples on the top were taken as soon as prepared, and the bottom ones were taken after 15 min. Concentrations: 1 mg/mL.

Figure S5. Dispersion stabilities of **TPE-C_4N_3-G-In** (top) and graphene (bottom) in toluene, DMF, $CHCl_3$, ethanol and acetone (from left to right) with sonication for 5 min. The photographs were taken 1 hour later. Concentrations: 1 mg/mL.

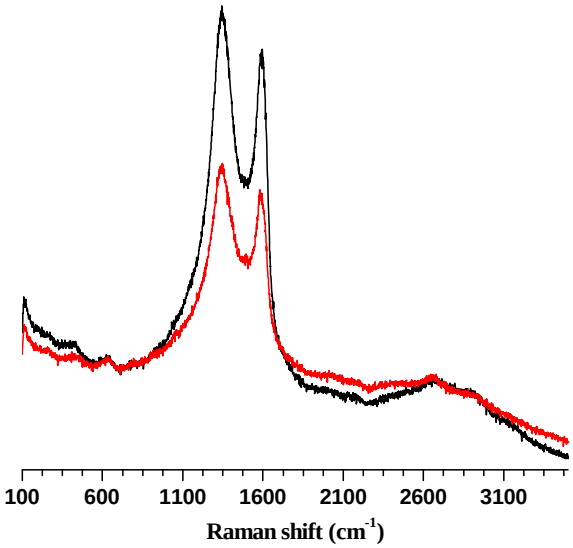


Figure S6. Raman spectra of graphene (blank) and **TPE-C_4N_3-G-In** (red).

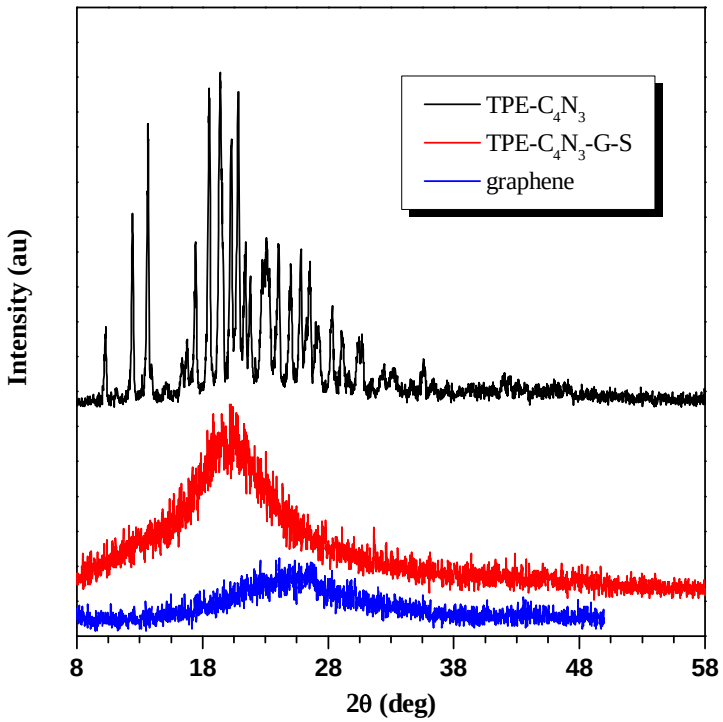


Figure S7. XRD patterns of **TPE-C_4N_3**, graphene and **TPE-C_4N_3-G-S**.

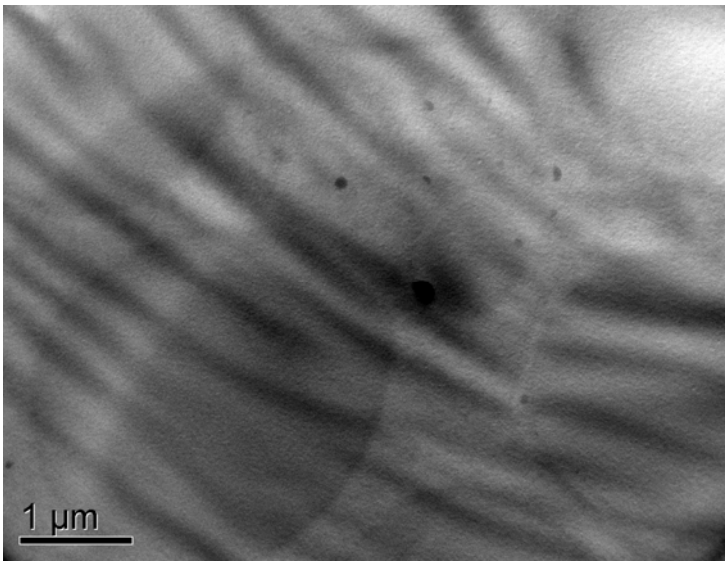


Figure S8. TEM image of **TPE-C_4N_3**.

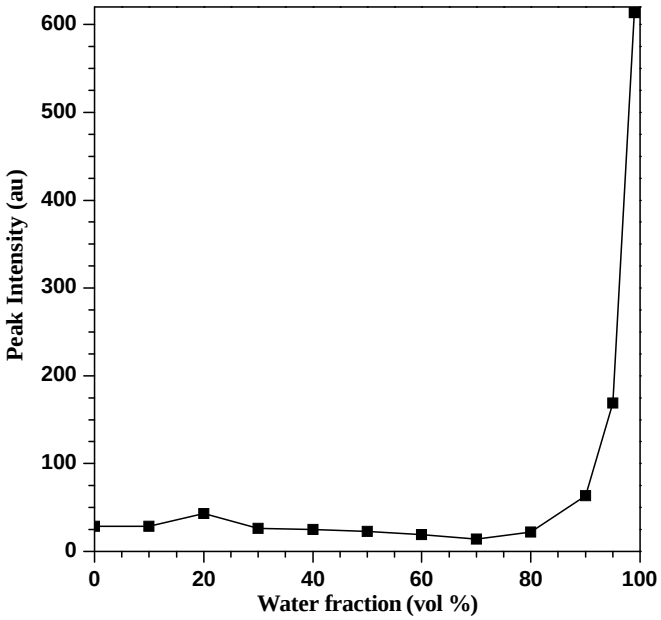


Figure S9. Changes in the PL peak intensities of **TPE-C_4N_3** with different water fractions in the H_2O/THF mixture. Concentrations: 10 μM. Excitation wavelength: 330 nm.

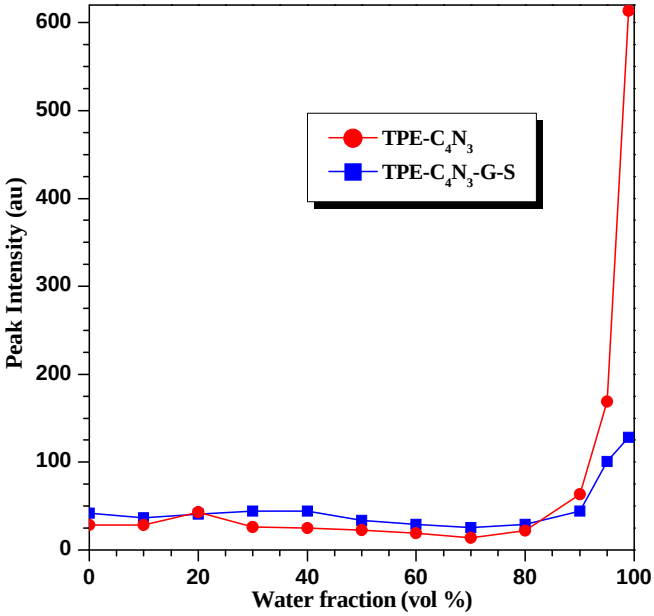


Figure S10. Changes in the PL peak intensities of **TPE-C_4N_3-G-S** and **TPE-C_4N_3** with different water fractions in the H_2O/THF mixture. Concentrations: 10 μM. Excitation wavelength: 330 nm.

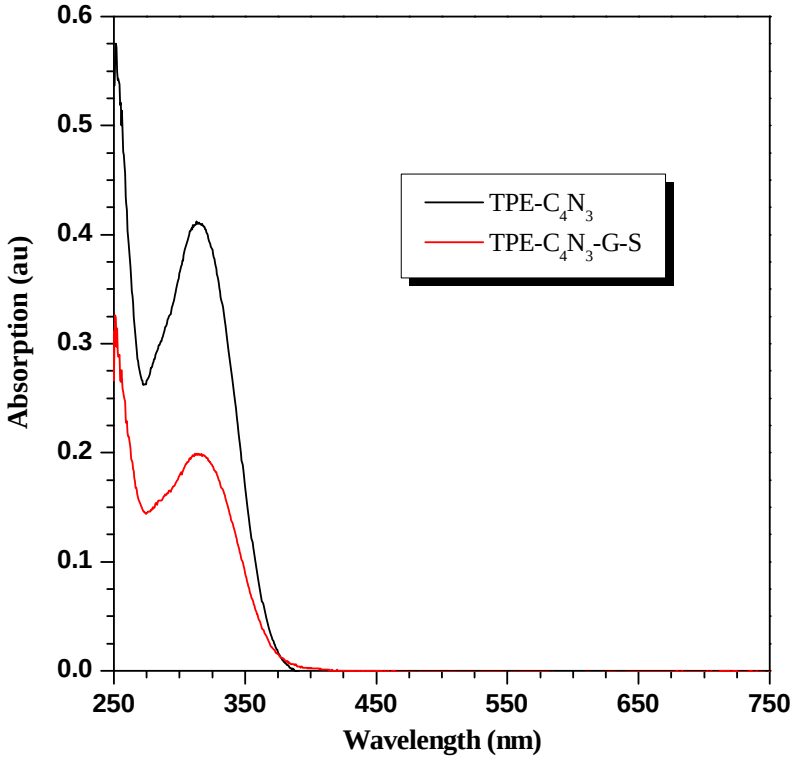


Figure S11. UV-vis spectra of **TPE-C_4N_3** and **TPE-C_4N_3-G-S** in THF.

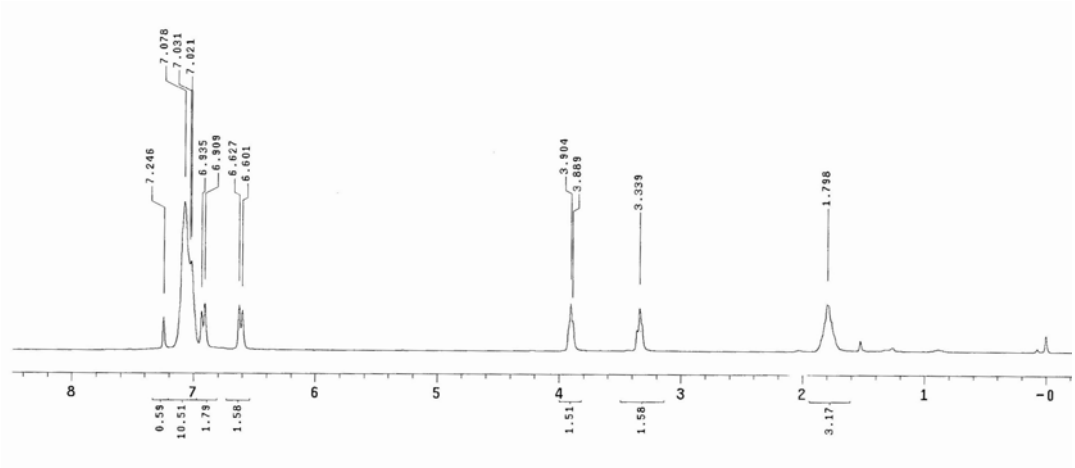


Figure S12. ^{1}H NMR of **TPE-C_4N_3**.

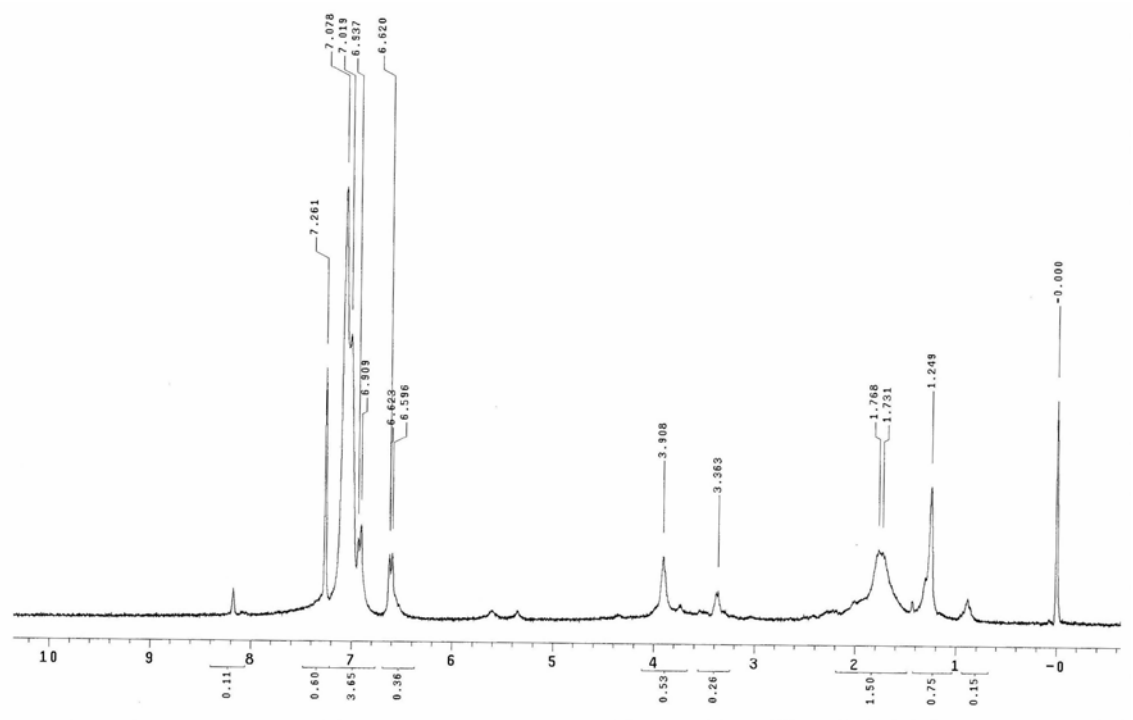


Figure S13. ^{1}H NMR of **TPE-C$_4$N$_3$-G-S**.

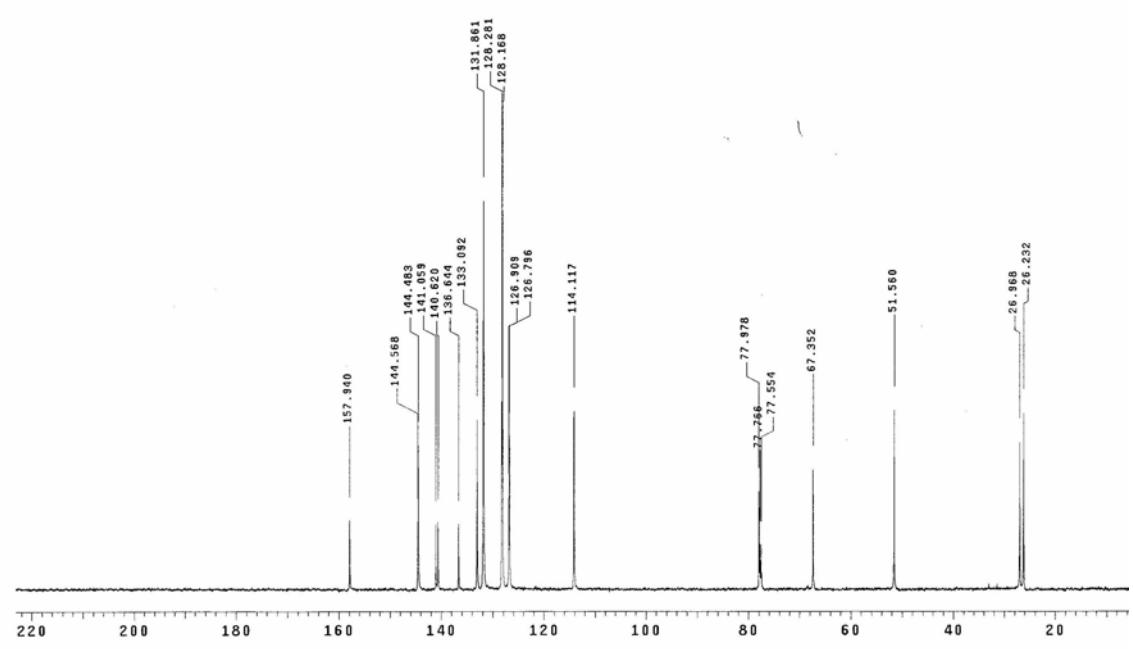


Figure S14. ^{13}C NMR of **TPE-C$_4$N$_3$**.

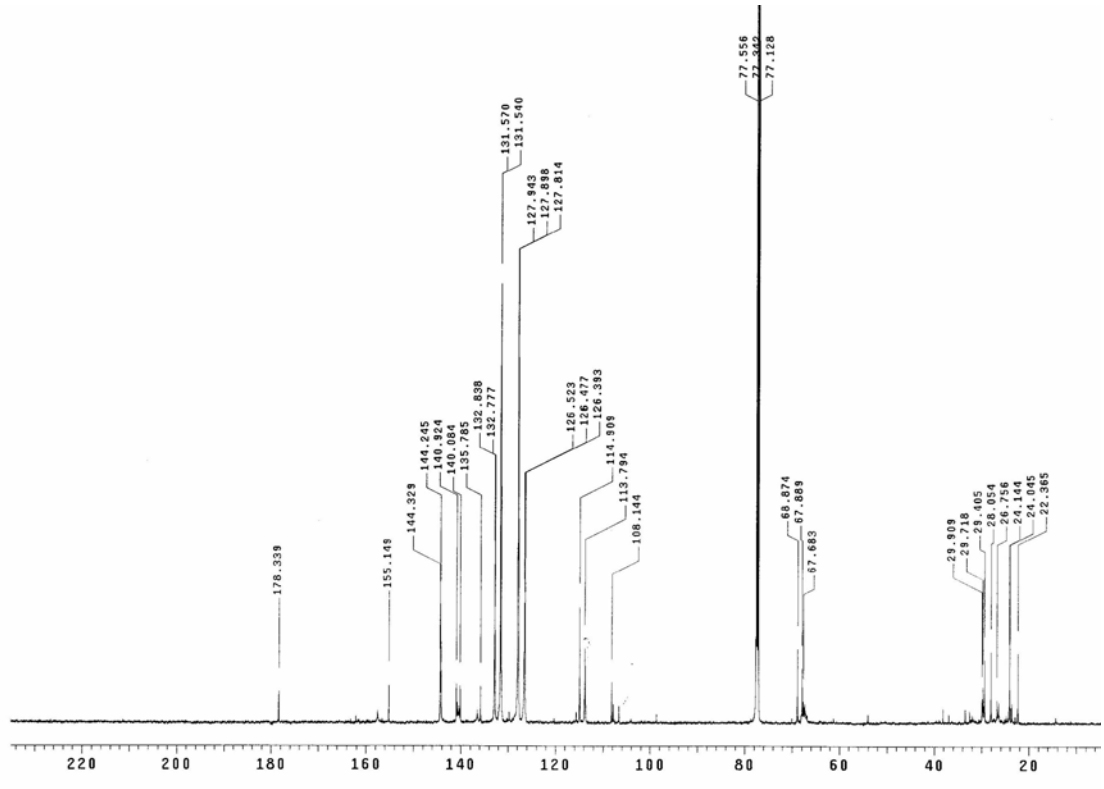


Figure S15. ^{13}C NMR of **TPE-C_4N_3-G-S**.

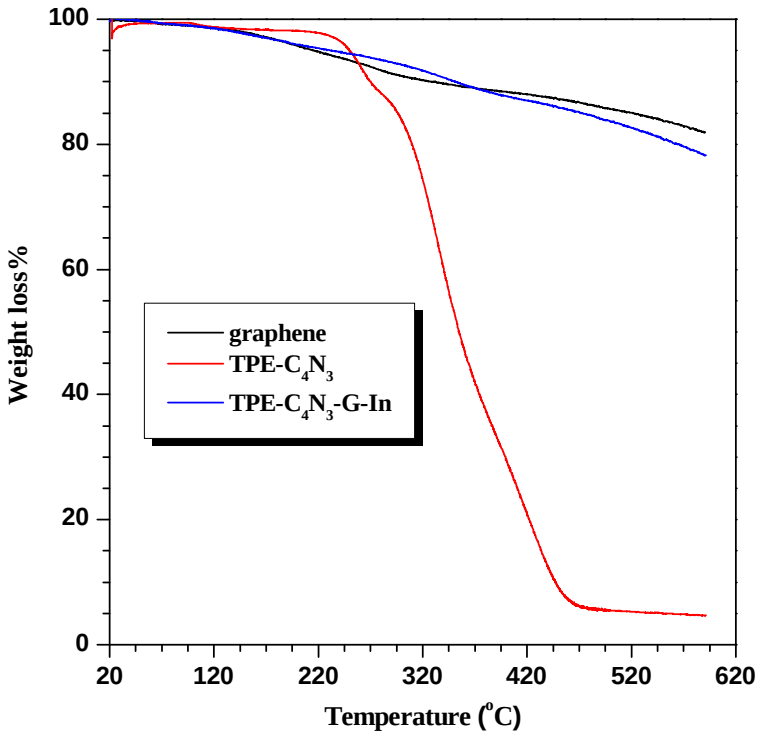


Figure S16. Thermo-gravimetric analyses of graphene, **TPE-C_4N_3** and **TPE-C_4N_3-G-In**.

Figure S17. Photographs of the reaction system of **TPE-C_4N_3-G**, **PB-G** and **TPP-C_4N_3-G**, and the photographs were taken after one week.

Reference

(1) Q. Zeng, Z. Li, Y. Dong, C. Di, A. Qin, Y. Hong, L. Ji, Z. Zhu, C. K. W. Jim, G. Yu, Q. Li, Z. Li, Y. Liu, J. Qin and B. Z. Tang, *Chem. Commun.*, 2007, 70-72.