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Functionalization of graphene by tetraphenylethylene using nitrene chemistry

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Experimental Section

Synthesis and Characterization

Synthesis of Compound S3

S1, S2, and S3 were prepared according to our previous work 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),
$\delta$ (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$_4$N$_3$. A white solid was obtained in 92% (852 mg). $^1$H NMR (CDCl$_3$, 300 MHz), $\delta$ (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$_2$Cl$_2$ (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), $\delta$ (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$_4$N$_3$. A yellow solid was obtained in 90% (530 mg).$^1$H NMR (CDCl$_3$, 300 MHz), $\delta$ (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$_4$N$_3$-G**

The procedures were similar to that of TPE-C$_4$N$_3$-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$_4$N$_3$-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$_4$N$_3$-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-C₄N₃-G-In (top) and graphene (bottom) in toluene, DMF, CHCl₃, 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-C₄N₃-G-In (red).
Figure S7. XRD patterns of TPE-C₄N₃, graphene and TPE-C₄N₃-G-S.

Figure S8. TEM image of TPE-C₄N₃.
Figure S9. Changes in the PL peak intensities of TPE-C$_4$N$_3$ with different water fractions in the H$_2$O/THF mixture. Concentrations: 10 μM. Excitation wavelength: 330 nm.

Figure S10. Changes in the PL peak intensities of TPE-C$_4$N$_3$-G-S and TPE-C$_4$N$_3$ with different water fractions in the H$_2$O/THF mixture. Concentrations: 10 μM. Excitation wavelength: 330 nm.
**Figure S11.** UV-vis spectra of TPE-C₄N₃ and TPE-C₄N₃-G-S in THF.

**Figure S12.** ¹H NMR of TPE-C₄N₃.
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$_4$N$_3$-G-S.

**Figure S16.** Thermo-gravimetric analyses of graphene, TPE-C$_4$N$_3$ and TPE-C$_4$N$_3$-G-In.
Figure S17. Photographs of the reaction system of TPE-C₄N₃-G, PB-G and TPP-C₄N₃-G, and the photographs were taken after one week.

Reference