

Electronic Supplementary Information (ESI)

Photoactive Graphene Sheets Prepared by “Click” Chemistry

Hang-Xing Wang, Kai-Ge Zhou, Yu-Long Xie, Jing Zeng, Na-Na Chai, Jun Li and Hao-Li Zhang*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering,
Lanzhou University, Lanzhou, 730000, China

*Email: haoli.Zhang@lzu.edu.cn

Experimental section

Materials

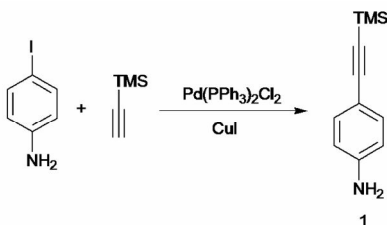
Graphite flake (natural, ~325 meshes, 99.8%) was purchased from ABCR GmbH (Germany). All chemicals and solvents were obtained commercially and used without further purification unless otherwise noted. De-ionized water (18.2 MΩ) was used throughout the experiments.

Instruments

Transmission Electron Microscopy (TEM) images were performed on Tecnai G2 F30 electron microscope operating at 300 kV. Atomic Force Microscopy (AFM) images were performed using an Agilent SPM 5500 in the tapping mode. Scanning Electron Microscopy (SEM) was performed on Hitachi S4800. Fourier Transform Infrared Spectra (FTIR) was obtained on a Bruker V70 spectrometer. Raman spectra were obtained by in Via Reinshaw confocal spectroscopy with 633nm laser excited. X-ray Photoelectron Spectroscopy (XPS) analyses were carried on a PHI-5702 X-ray photoelectron spectrometer. UV-Vis absorption spectra were recorded using a T6 UV-Vis spectrometer (Purkinje General, China). Fluorescence measurements were made using a LS55 fluorescence spectrometer (PE, USA). Photo-current response measurement was conducted using a CHI660B electrochemistry work station (CHI, USA). A three-electrode configuration consisting of an indium tin oxide (ITO) as working electrode, a platinum wire as counter electrode, and saturated calomel electrode as reference electrode. KCl (0.5 M) aqueous solution was the electrolyte solution. The samples were prepared by spin-casting graphene-based materials (ZnP-GS, RuP-GS and GS) onto the ITO electrode (1.0 cm×1.0 cm). A 500W Xe lamp was used as the light source. ¹H-NMR

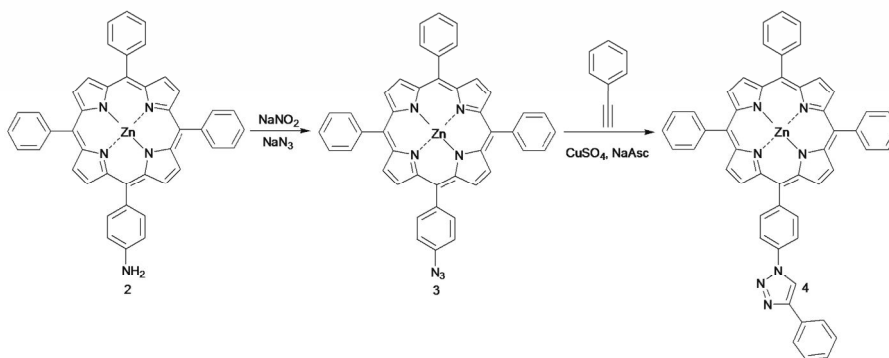
spectra were recorded with a Bruker 400 MHz spectrometer with tetramethylsilane (TMS) as the internal standard. Electrospray ionization (ESI) mass spectra were measured on a Bruker Esquire 6000 instrument.

Synthesis



Scheme S1 Synthesis route of 4-(2-trimethylsilyl)-ethynylaniline 1.

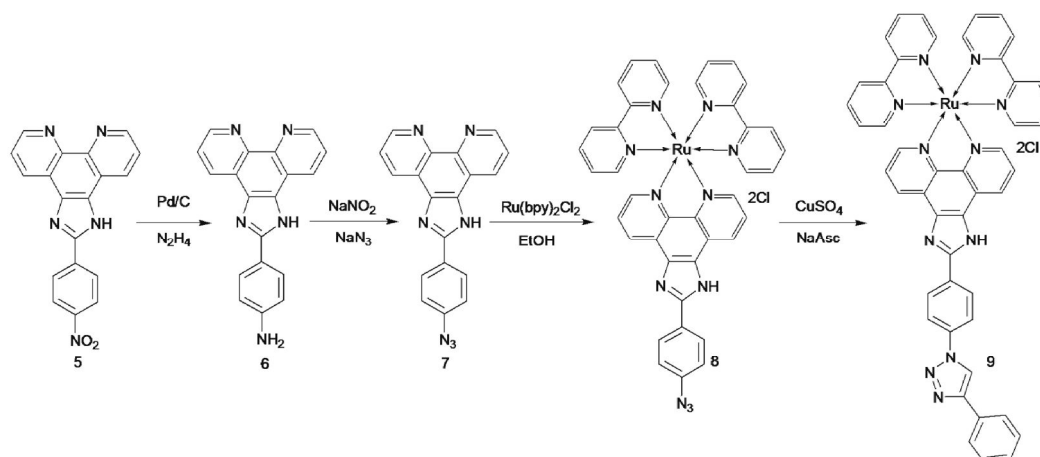
4-(2-trimethylsilyl)-ethynylaniline 1. 4-iodoaniline (1.0 g, 4.56 mmol), bistriphenylphosphine palladium (II) chloride (88 mg, 0.126 mmol), and CuI (22 mg, 0.115 mmol) were added to a round bottomed flask. The mixture was purged with N₂ and dry tetrahydrofuran (THF, 25 mL) was added via syringe. The trimethylsilyl acetylene (0.78 mL, 5.5 mmol) was subsequently added via syringe and the reaction mixture was stirred for 0.5 h. Then triethylamine (25 mL) was added via syringe and the mixture was stirred at room temperature for 12 h. The THF and triethylamine were removed under vacuum and the brown solid mixture was separated by column chromatography (silica gel) with a solvent system of petroleum ether (PE)/dichloromethane (DCM) = 2/1 (v/v) to afford a light yellow solid (0.53 g, 62% yield). ¹H-NMR (CDCl₃) δ 7.27 (d, 2H, J = 8.8 Hz), 6.57 (d, 2H, J = 8.4 Hz), 3.87 (s, 2H), 0.224 (s, 9H). MS (ESI): C₁₁H₁₅NSi (189.1) m/z = 190.1 [M⁺].



Scheme S2 Synthesis route of zinc porphyrin derivatives.

Azide-terminated zinc-porphyrin (Zn-P-N₃) 3. Hydrochloric acid (10%, 1 mL, v/v) was added to a stirred solution of amino-terminated zinc-tetraphenyl-porphyrin 2¹ (200 mg, 0.288 mmol) in THF/H₂O (20 mL, v/v = 9/1). NaNO₂ (19.9 mg, 0.288 mmol) dissolved in deionized water (0.5 mL) was added. The mixture was stirred for 10 min at 0°C. A solution of NaN₃ (18.7 mg, 0.288 mmol) in deionized water (0.5 mL) was added dropwise and the reaction was carried on under stirring for 30 min. The equal amount of NaN₃ (18.7 mg, 0.288 mmol) in deionized water (0.5 mL) was added dropwise and the reaction stirred for 2 h. The solution was diluted with deionized water (5 mL) and extracted with DCM (3×15 mL). And then the organic layer was washed with saturated NaHCO₃ (15 mL). The organic layer was collected and the solvent removed by rotary evaporator. The deep purple solid (120 mg, 58% yield) was separated by column chromatography with a solvent system of PE/DCM (1/1, v/v). ¹H-NMR (400 MHz, CDCl₃) δ 8.96-8.92 (m, 8H, β-pyrrolic), 8.23-8.18 (m, 8H), 7.78-7.73 (m, 9H), 7.37 (d, 2H, J = 8.00 Hz). MS (ESI): C₄₄H₂₇N₇Zn (717.2) m/z = 717.3 [M⁺].

Reference molecule zinc-porphyrin-triazole-phenyl (ZnP) 4. CuSO₄·5H₂O (7.5 mg, 0.03 mmol) and sodium ascorbate (30.1 mg, 0.15 mmol) were added to a solution of 3 (245.0 mg, 0.34 mmol) in a mixture THF/H₂O (66mL, v/v=10/1). The oxygen was removed by bubbling with N₂ for 20 min, phenylacetylene (80μL, 0.68 mmol) was added and the reaction mixture was protected by N₂. Finally, the solution was stirred at 50°C for 24 h, then water was added, and the mixture was extracted with DCM; The solvents was dried by rotary evaporator and the pure red purple solid product was obtained by column chromatography (silica gel) and DCM as eluent (221.2 mg, 79% yield). ¹H-NMR (400 MHz, CDCl₃) δ 9.01 (d, 2H, J = 4.8 Hz), 8.98-8.94 (m, 6H), 8.44 (s, 1H), 8.41 (d, 2H, J = 8.0 Hz), 8.25 (d, 6H, J = 7.2 Hz), 8.16 (d, 2H, J = 8.0 Hz), 7.95 (d, 2H, J = 7.2 Hz), 7.80-7.75 (m, 9H), 7.49 (t, 2H, J = 7.6 Hz), 7.40 (t, 1H, J = 7.6 Hz). MS (ESI): C₅₂H₃₃N₇Zn (821.5) m/z = 822.5 [M⁺].



Scheme S3 Synthesis route of ruthenium-phenanthroline derivatives.

2-(4-aminophenyl)imidazo[4,5-f][1,10]phenanthroline (P-NH₂) 6. A mixture of 2-(3-nitrophenyl)imidazo[4,5-f][1,10]phenanthroline (P-NO₂, 5)² (400 mg, 1.17 mmol) was completely dissolved in methanol (MeOH, 100 mL) with stirring for 1 h. Then the Pd/C (0.40 g, 10% Pd) and hydrazine hydrate (10 mL) were added in the above solution and refluxed for 4 h, then cooled to room temperature and stirred for 2 h. The solution was filtered and evaporated to remove the solvent under reduced pressure. The pale yellow compound was obtained by recrystallization with ethanol (EtOH). Yield: (218.3 mg, 60.0%). ¹H-NMR (400 MHz, DMSO-d₆): δ 13.50 (s, NH), 8.99 (broad s, 2H), 8.89 (d, 2H, J = 8.0 Hz), 7.98 (d, 2H, J = 8.0 Hz), 7.80-7.79 (m, 2H), 6.74 (d, 2H, J = 8.8 Hz), 5.66 (s, 2H, H-NH₂). MS (ESI): C₁₉H₁₃N₅ (311.2) m/z = 312.2 [(M+H)⁺].

2-(4-azidophenyl)imidazo[4,5-f][1,10]phenanthroline (P-N₃) 7. To a stirred solution of 6 (200 mg, 0.64 mmol) in H₂O (20 mL) was added a solution of hydrochloric acid (1 mL, 10%, v/v) stirred for 20 min at 0°C. NaNO₂ (44.9 mg, 0.65 mmol) dissolved in deionized water (1.0 mL) was added. The mixture was stirred for 10 min at 0 °C. A solution of NaN₃ (41.6 mg, 0.64 mmol) in deionized water (1.0 mL) was added dropwise and the reaction was carried on under stirring for 30 min. The equal amount of NaN₃ (41.6 mg, 0.64 mmol) in deionized water (1.0 mL) was added dropwise and the reaction stirred for 2 h. The solution was neutralized with ammonia and the solution was filtered, and then the obtained solid was washed with H₂O. The pale yellow compound was obtained by recrystallization with MeOH.

Yield: (114.9 mg, 53%). $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 13.86 (s, H-NH), 9.03-9.02 (m, 2H), 8.93 (broad s, 2H), 8.32 (d, 2H, $J = 8.4$ Hz), 7.86 (broad s, 2H), 7.34 (d, 2H, $J = 8.4$ Hz). MS (ESI): $\text{C}_{19}\text{H}_{13}\text{N}_5$ (337.2) $m/z = 338.2$ $[(\text{M}+\text{H})^+]$.

Azide-terminated ruthenium-phenanthroline derivative ($\text{Ru}(\text{bpy})_2\text{-P-N}_3$) 8. A mixture of Ruthenium-2,2'-bipyridine complex ($\text{Ru}(\text{bpy})_2\text{Cl}_2$, 242 mg, 0.5 mmol) and 7 (166 mg, 0.5 mmol) in ethanol (30 mL) was refluxed under N_2 for 8 h to give a red solution and was then filtered to remove unreacted starting materials. The filtrate was concentrated under vacuum and then poured into Et_2O (50 mL). The solution was filtered, and the obtained solid was washed with Et_2O . The crude product was dried to give compound. The crude product was purified by column chromatography on a neutral alumina with a mixture of acetonitrile-toluene-ethanol (100/50/1, v/v) as eluant. The mainly red band was collected. The solvent was removed under reduced pressure and a red powder was obtained as magenta solid (258 mg, 63% yield). $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 9.05 (d, 2H, $J = 8.6$ Hz), 8.88-8.93 (m, 6H), 8.34 (d, 2H, $J = 8.4$ Hz), 8.12 (t, 4H, $J = 7.7$ Hz), 8.00 (d, 4H, $J = 8.2$ Hz), 7.88 (broad s, 2H), 7.38 (t, 4H, $J = 7.7$ Hz), 7.35 (d, 2H, $J = 8.4$ Hz). MS (ESI): $\text{C}_{39}\text{H}_{27}\text{N}_{11}\text{RuCl}_2$ (821.4) $m/z=375.2$ $[(\text{M}-2\text{Cl})^{2+}]$.

Reference molecule ruthenium-phenanthroline-triazole-phenyl (RuP) 9. To a solution of 8 (328mg, 0.4 mmol) in a mixture $\text{EtOH}/\text{H}_2\text{O}$ (160mL, 10/1, v/v) were added $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (4 mg, 0.016 mmol) and sodium ascorbate (5.96 mg, 0.030 mmol). The oxygen was removed by bubbling with N_2 for 20 min, and the reaction mixture was several cycles of vacuum/ N_2 then added phenylacetylene (80 μL , 0.68 mmol). Finally, the solution was stirred at 50°C for 24 h and was then filtered to remove unreacted starting materials 8. The filtrate was concentrated under vacuum and then poured into Et_2O (100 mL). The solution was filtered, and the obtained solid was washed with diethyl ether (Et_2O). The product was dried to give compound as magenta solid. The crude product was purified by column chromatography on a neutral alumina with a mixture of acetonitrile-toluene-ethanol (100/100/1, v/v) as eluant. The mainly red band was collected. The solvent was removed under reduced pressure and a red powder was obtained (0.21 g, 71%). $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ 9.50 (broad s, 1H),

8.93-8.88 (m, 6H), 8.59 (s, 1H), 8.22-8.16 (m, 6H), 8.11 (broad s, 2H), 8.03-8.00 (m, 2H), 7.85-7.84 (m, 4H), 7.74-7.72 (d, 2H, $J = 5.2$ Hz), 7.63-7.60 (m, 4H), 7.56-7.52 (m, 2H), 7.35 (broad s, 2H), 6.71 (broad s, 1H). MS (ESI): $C_{47}H_{33}N_{11}RuCl_2$ (923.1) $m/z = 852.2 [(M-2Cl)^+]$, 426.7 $[(M-2Cl)^{2+}]$.

Preparation of graphene oxide (GO). GO was prepared from natural graphite powder using the modified Hummers and Offenman's method with H_2SO_4 and $KMnO_4$.³ As-prepared GO was suspended in ultra-pure water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids for one week. The resulting purified graphene oxide powders were dried by P_2O_5 under vacuum for two weeks.

Preparation of GS. GO (30mg) was dispersed in H_2O/DMF (100mL, 1/9, v/v) and homogenized using ultrasonic at 200W power for 10 min. The pH was adjusted to 10 using ammonia water. The resulting GO dispersion was reduced with 80% hydrazine hydrate (300 μ L, 12.84 mmol) at 100°C under N_2 for 24 h followed by centrifugation (3000 rpm, 20 min) to remove large aggregates, yielding GS dispersion decant with a typical concentration of 0.3 mg/mL.

Preparation of T-GS. A suspension of GS dispersion (15 mg) in N-methylpyrrolidone (NMP, 60 mL) and **1** (475 mg, 2.5 mmol, 2eq C) was first added and then the suspension was sonicated for 30 min. After transfer to a septum-capped flask and bubbling with N_2 for 20 min, isoamyl nitrite (400 μ L, 3 mmol, 2.4eq C) were quickly added and the reaction mixture was stirred at 70°C overnight under N_2 . After cooling to room temperature, the suspension was filtered on a polytetrafluoroethylene (PTFE) membrane and the black solid was washed several times with DMF/DCM (1/1, v/v) until the unreacted **1** was completely removed (monitored by thin layer chromatography). The suspension was sonicated and redispersed in NMP (60 mL), and the entire procedure was repeated another time. A small part (1.0 mg) of the solid on the filter was collected for analyses and the rest was redispersed in DMF.

In situ deprotection of 4-(2-trimethylsilyl) ethynyl-GS (T-GS). To a suspension of T-GS

(15 mg) in DMF (40 ml) at 0°C was added a solution of tetrabutylammonium fluoride (NBu₄F, 1 M in THF, 20 µL). The reaction mixture was stirred at room temperature for 2 h then used directly for the next step.

Preparation of ZnP-GS. To a suspension of deprotected T-GS (15 mg) in DMF (40 ml) were added 3 (30 mg, 41.5 µmol), CuSO₄·5H₂O (3.6 mg, 12.4 µmol) and sodium ascorbate (24.8 mg, 125.2 µmol). After bubbling with N₂ for 20 min and the reaction mixture was stirred at 50°C for 36 h under argon and then filtered on a PTFE membrane. In order to remove sodium ascorbate, copper catalyst and free porphyrin, the black solid was sonicated and washed with mixture of DMF/water (1/4, v/v) and DMF/THF (1/4, v/v), and then filtered. These operations were repeated several times and the ZnP-GS finally washed with THF and DCM. These operations were repeated until the filtrate contained no porphyrin (checked by TLC and UV-Vis absorption).

Preparation of RuP-GS. To a suspension of deprotected T-GS (15 mg) in DMF/H₂O (40 ml, 9/1, v/v) were added 8 (34.1 mg, 41.5 µmol), CuSO₄·5H₂O (3.6 mg, 12.4 µmol) and sodium ascorbate (24.8 mg, 125.2 µmol). After bubbling with N₂ for 20 min and the reaction mixture was stirred at 50°C for 36 h under argon and then filtered on a PTFE membrane. In order to remove sodium ascorbate, copper catalyst and free 8, the black solid was sonicated and washed with mixture of DMF/water (4/1, v/v) and then filtered. These operations were repeated several times and the RuP-GS finally washed with EtOH. These operations were repeated until no 8 was contained in filtrate (checked by UV-Vis absorption).

Characterization

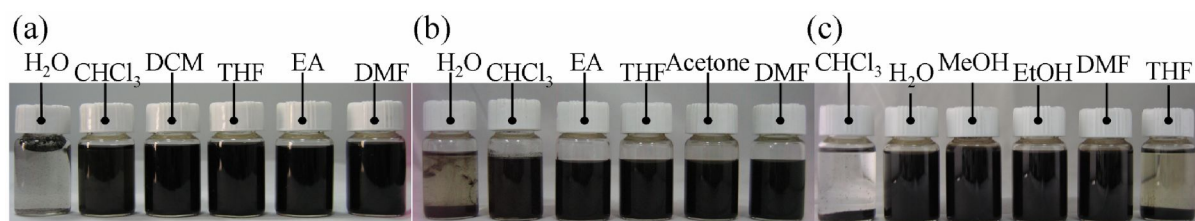


Fig. S1 Photographs of (a) T-GS, (b) ZnP-GS and (c) RuP-GS in various solvents.

The first and simplest qualitative test to determine the successful chemical modification involved checking dispersibility of the product in common solvents. Fig. S1 shows three types of samples containing equal masses of (a) T-GS, (b) ZnP-GS and (c) RuP-GS in various solvents. It is found that the (a) T-GS, (b) ZnP-GS and (c) RuP-GS samples exhibited good dispersibility in solvents known to effectively solvate the attached molecular fragment. Conversely, any solvent in which the molecule does not dissolve was also incapable of dissolving the GS conjugates. The T-GS and ZnP-GS conjugates can be readily dispersed in some common organic solvents such as CHCl_3 , ethyl acetate (EA), THF, DMF, DCM and Acetone but exhibited poor solubility in H_2O . The RuP-GS conjugate (Fig. S1c) has a good dispersibility in H_2O , MeOH, EtOH, DMF but exhibited poor solubility in THF and CHCl_3 .

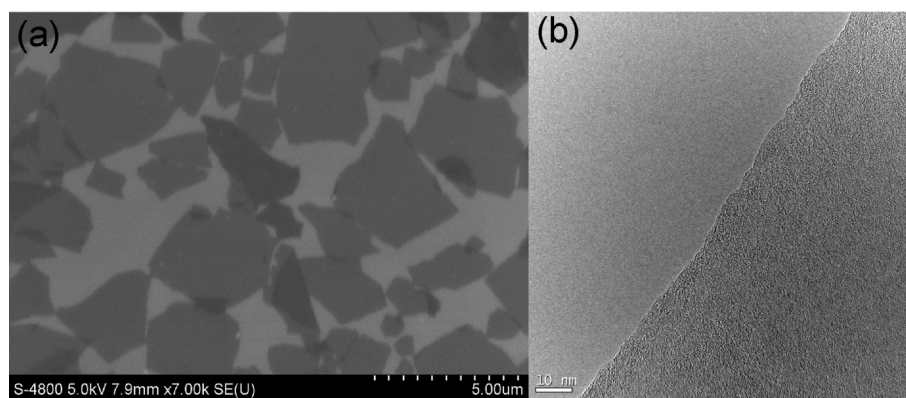


Fig. S2 (a) SEM image of T-GS on SiO_2/Si substrate and (b) High resolution TEM image of T-GS.

Fig. S2a is a representative SEM image of T-GS deposited on SiO_2/Si substrate from solution, which shows the sizes of the sheets are generally around several microns. Fig. S2b presents the HR-TEM of T-GS on copper grid, which shows that the sheet exists as monolayer. These images revealed that the T-GS sample prepared under our condition mostly exists as large monolayer sheets with the width of several microns.

Fig. S3a shows FTIR spectrum of the covalent attachment of RuP onto GS surface via “click” chemistry. GO (black curve) shows the peaks at 1060, 1250, and 1365 cm^{-1} indicates the epoxide and the hydroxyl groups attached to the basal graphene layer.⁴ For RuP-GS (red curve), the characteristic signals for RuP as compared with the spectrum of RuP (green curve, dotted line show $720.7, 800.6, 840.6\text{ cm}^{-1}$), indicating that RuP had been grafted. The

noticeably appearance of triazole signals at 1095 and 1455 cm^{-1} (triazole ring stretching vibrations), indicates that most of the alkynes have been converted to triazole bonds during this reaction. These results clearly indicated that the RuP molecules had been covalently bonded to GS via the “click” chemistry.

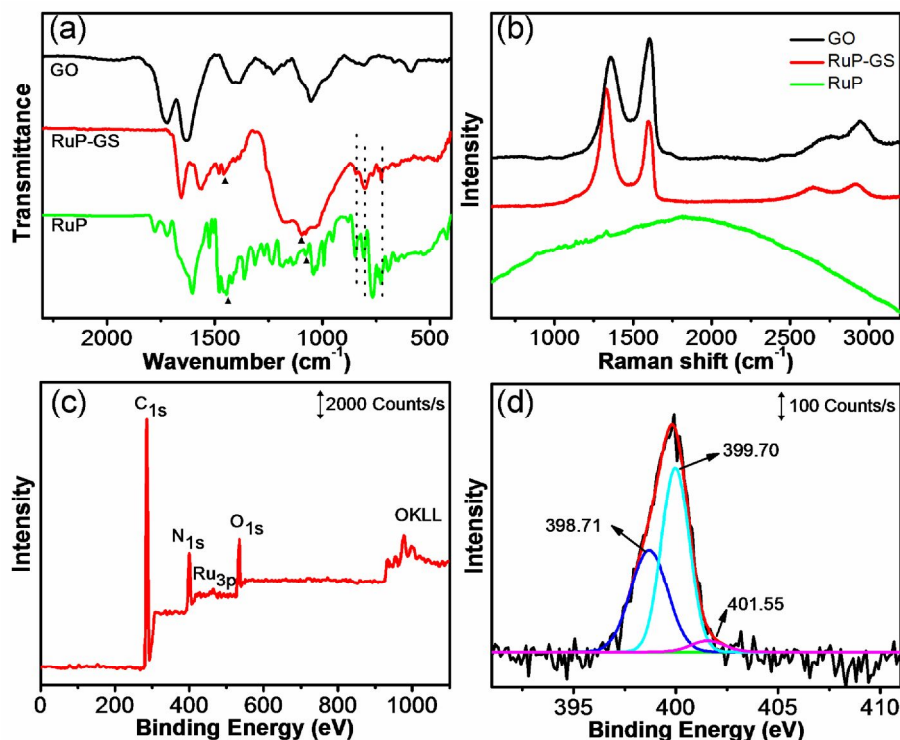


Fig. S3 (a) FTIR and (b) Raman spectra of GO, RuP-GS and reference molecule RuP. (\blacktriangle) shows the triazole ring stretching vibrations signal, Raman spectra recorded after excitation at 633 nm. (c) XPS spectra of RuP-GS and (d) N_{1s} XPS spectrum of the RuP-GS.

Fig. S3b shows Raman spectrum of GO (black curve), RuP-GS (red curve) and RuP (green curve). GO contains both D and G bands (at 1352 and 1584 cm^{-1} , respectively). The intensity ratio of D band to G band (I_D/I_G) of GO is ~ 0.82 , which is consistent with previous report.⁵ The Raman spectrum of RuP-GS is almost identical to that of T-GS, thus implying that no further structural perturbation of the graphene skeleton occurred upon treatment of the deprotected T-GS with azide-terminated ruthenium-phenanthroline derivative. The Raman spectrum of RuP can hardly be observed due to the strong luminescence from RuP.

XPS spectra recorded for RuP-GS (Fig. S3c) give rise to the spectroscopic signature of

carbon, oxygen, nitrogen and ruthenium. The Ru_{3p3/2} band appearing at a binding energy of 462.59 eV.⁶ This XPS data proves the presence of RuP derivative in the RuP-GS, in accordance with the FTIR and Raman results. The N_{1s} band of the sample shows the diagnostic signature of the nitrogen atoms as part of the formed triazole ring, the lack of a peak corresponding to free azide groups at 405.0 eV unambiguously indicates that azide-terminated ruthenium-phenanthroline derivative was covalently attached to the GS surface via a triazole ring and was not simply physisorbed on the surface by π -stacking interaction. Analysis of the Ru_{3p3/2} region of RuP-GS and the calculation of the ratio of (Ru_{3p3/2}/C_{1s}) allows us to determine the number of functional groups on the GS surface. A quantitative analysis of the XPS data in the Ru_{3p3/2} and C_{1s} regions allows us to estimate the ratio of the attached RuP group and the graphene carbon atom, which give 1: 88 (Table S3).

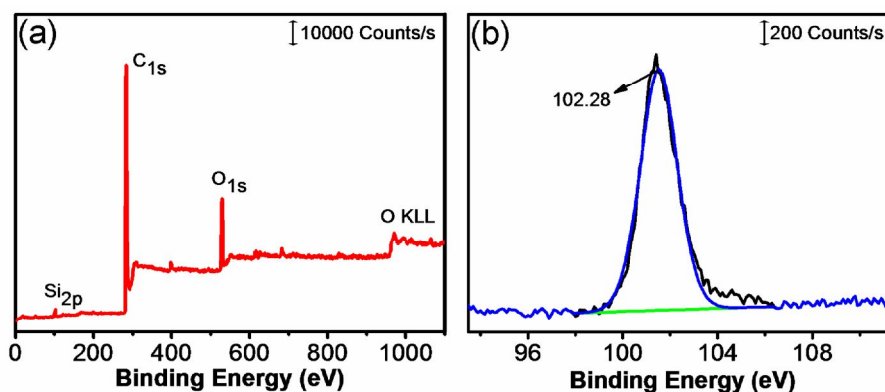


Fig. S4 (a) XPS spectra of T-GS, (b) Si_{2p} XPS of T-GS supported on polytetrafluoroethylene (PTFE) membrane.

The quantitative contents of alkyne, ZnP and RuP moieties were calculated from the XPS spectra of the T-GS, ZnP-GS and RuP-GS samples. Based on the atomic ratio of C to Si as determined from the C_{1s} and Si_{2p} peaks (Fig. S4 and Table S1), we determine the number of functional trimethyl-(phenylethynyl)-silane (C₁₁H₁₃Si) unites on the T-GS surfaces by the calculation: $N_C = (83.56 - 0.92 \times 11) / 0.92 = 79.8$, which means that one alkyne group is covalently attached with ~ 80 carbon atoms in the T-GS complex.

Using the same calculation method, from the atomic ratio of C to Zn in the ZnP-GS complex (Table S2), we can obtain that one ZnP molecule (C₅₂H₃₃N₇Zn) is covalently

attached with ~ 108 carbon atoms in the ZnP-GS complex ($N_C = (79.92 - 0.5 \times 52) / 0.50 = 107.84$).

Similarly, from the atomic ratio of C to Ru in the RuP-GS complex (Table S3), we obtained that each RuP is attached with ~ 88 carbon atoms in the RuP-GS complex ($N_C = (79.59 - 0.59 \times 47) / 0.59 = 88$).

Table S1 XPS results of T-GS			Table S2 XPS results of ZnP-GS			Table S3 XPS results of RuP-GS		
Core level	Position/eV	%Conc.	Core level	Position/eV	%Conc.	Core level	Position/eV	%Conc.
C _{1s}	284.83	83.56	C _{1s}	284.81	79.92	C _{1s}	285.19	79.59
O _{1s}	531.73	8.79	N _{1s}	400.46	8.53	N _{1s}	399.59	10.12
Si _{2p}	102.28	0.92	O _{1s}	532.31	9.48	O _{1s}	531.59	9.69
			Zn _{2p_{3/2}}	1021.79	0.50	Ru _{3p_{3/2}}	462.59	0.59

These results indicate that nearly all the surface attached alkyne unites were converted into triazole moieties, which give high surface coverage of ZnP and RuP. It is concluded from the quantitative XPS analysis that our surface modification method is highly efficient.

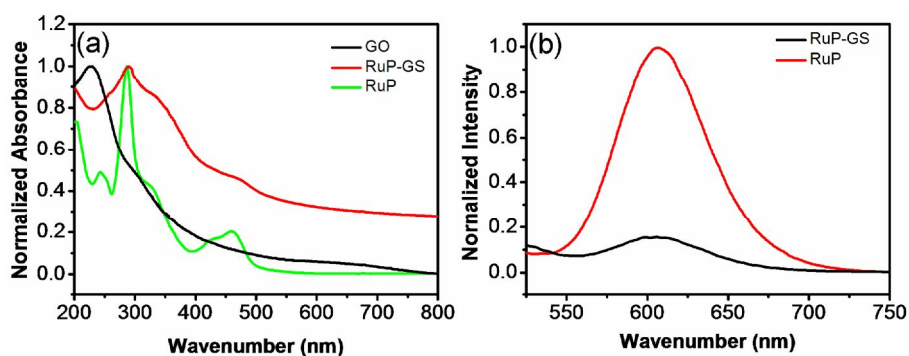


Fig. S5 UV-Vis absorption of GO, RuP-GS and RuP in H₂O, respectively. (b) Fluorescence spectra of RuP-GS and RuP in aqueous solution that exhibit the same optical absorption at the 440 nm excitation wavelength.

UV-Vis absorption spectra of GO (black curve), RuP-GS (red curve) and RuP (green curve) in H₂O are illustrated in Fig. S5a. The lack of any absorption band and the low scattering effect that is observed in the UV-Vis spectra of GO. The spectra of RuP-GS shows mainly absorption bands at 290 and ~ 397 -524 nm, and a red-shift about 3 nm is observed compared

to the absorption bands of RuP (287 nm, 394-521 nm), indicating not only the linkage of RuP with GS but also electronic interactions between the two species (GS and RuP) in the ground state. Fig. S5b shows the fluorescence spectra of RuP-GS (black curve) and RuP (red curve). Upon excitation at 440 nm, the characteristic fluorescence emission of RuP at 605 nm in aqueous solution is significantly quenched in RuP-GS complex.

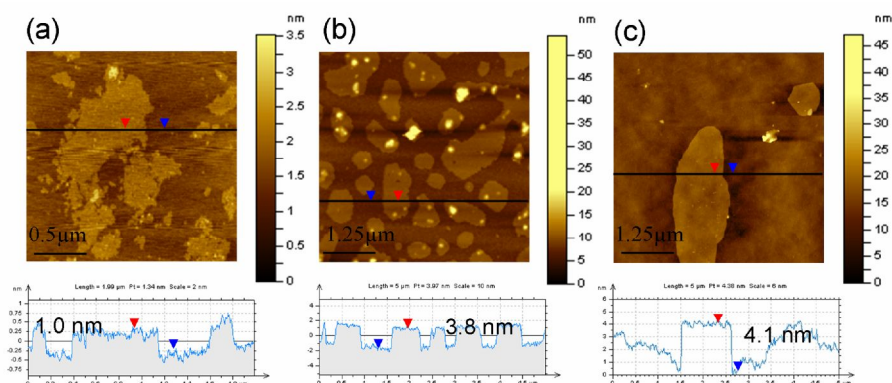


Fig. S6 Tapping mode AFM images of (a) GO, (b) ZnP-GS and (c) RuP-GS dispersions after deposition on freshly cleaved mica surfaces.

Individual functionalized GSs were imaged using tapping mode AFM. Fig. S6a shows the AFM image of GO, which exhibits an average thickness of ~ 1.0 nm, matching well with that of the single-sheet GO reported in the literatures.⁷ The AFM images of the functionalized GSs reveal that the heights of (b) ZnP-GS and (c) RuP-GS are ~ 3.8 nm and ~ 4.1 nm, respectively. When compared with well exfoliated GO sheets, the thickness of T-GS, ZnP-GS and RuP-GS are significantly increased as would be expected for the results of attaching of the phenylethynyl-trimethylsilane, ZnP and RuP onto both sheet sides.

The theoretical thicknesses of T-GS and ZnP-GS and RuP-GS have been estimated from the molecular mechanic (MM) simulation (Fig. S7), which give ~ 2.8 , ~ 5.6 and ~ 5.4 nm, respectively. The calculated thickness of T-GS is in good agreement with that observed by the AFM measurements, indicating that the T-GS sample is indeed composed of single layer of GS. However, the experimental observed layer thicknesses of ZnP-GS and RuP-GS are slightly lower than that expected from the theoretical calculation, which could be attributed to the slight titling of the attached functional groups. Never the less, the reasonably good

agreement between the theoretical thicknesses and that observed by the AFM measurement, which indicates that the ZnP-GS and RuP-GS samples are indeed composed of single layer of GSs.

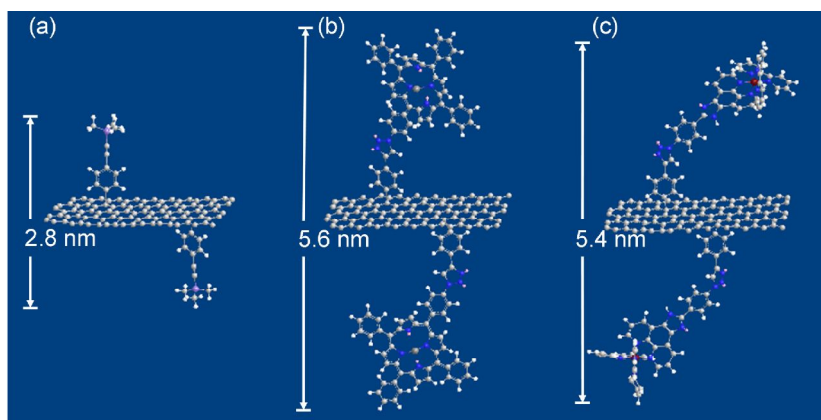


Fig. S7. Representation of the (a) T-GS, (b) ZnP-GS and (c) RuP-GS conjugates. The conformations of the molecules were modeled using Chem3D ultra 8.0 software and the distances were estimated from the terminal of the molecules to the closest carbon atom of the graphene surfaces.

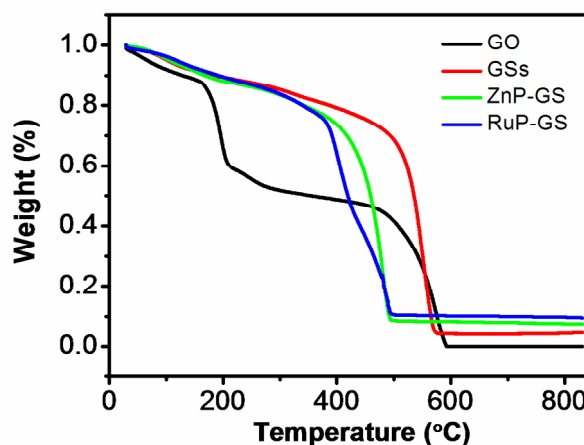


Fig. S8 TGA of GO (black curve), GS (red curve), ZnP-GS (green curve) and RuP-GS (blue curve) by heating under air atmosphere from room temperature to 830 °C at a rate of 10 °C/min.

As shown in Fig. S8, the TGA were performed on GO, GS, ZnP-GS and RuP-GS heated in a TGA instrument from room temperature to 830°C at heating rate of 10 °C min⁻¹ under air atmosphere. It was observed that GO is almost complete combustion of the material occurs

upon heating the sample in air, the residual weight being $\sim 0.5\%$, and there are two significant drops in mass around 190 and 522 $^{\circ}\text{C}$. The former is decomposition of the labile oxygen-containing functional groups, yielding CO , CO_2 , and steam, and the latter is attributed to pyrolysis of the carbon skeleton of GO. After using chemical method to reduce GO with hydrazine hydrate, the GS shows gradual weight loss in the temperature ranges from 150 to 300 $^{\circ}\text{C}$ and significant weight loss around 540 $^{\circ}\text{C}$, respectively. The former can be attributed mostly to the COOH groups that are incomplete dearomatized, and the latter can be attributed to the pyrolysis of the carbon skeleton of GS. In addition, the percentage of residual weight at 830 $^{\circ}\text{C}$ of ZnP-GS and RuP-GS are $\sim 8.1\%$ and $\sim 11.2\%$, respectively. They are both higher than that of GO ($\sim 0.5\%$) and GS ($\sim 5.1\%$). We attribute the increase in the non-carbonaceous material in ZnP-GS and RuP-GS to zinc oxides and ruthenium oxides arising from the combustion of ZnP-GS and RuP-GS. These are consistent with earlier reports for SWNTs covalently functionalized by porphyrin or ruthenium-phenanthroline complexes.⁶

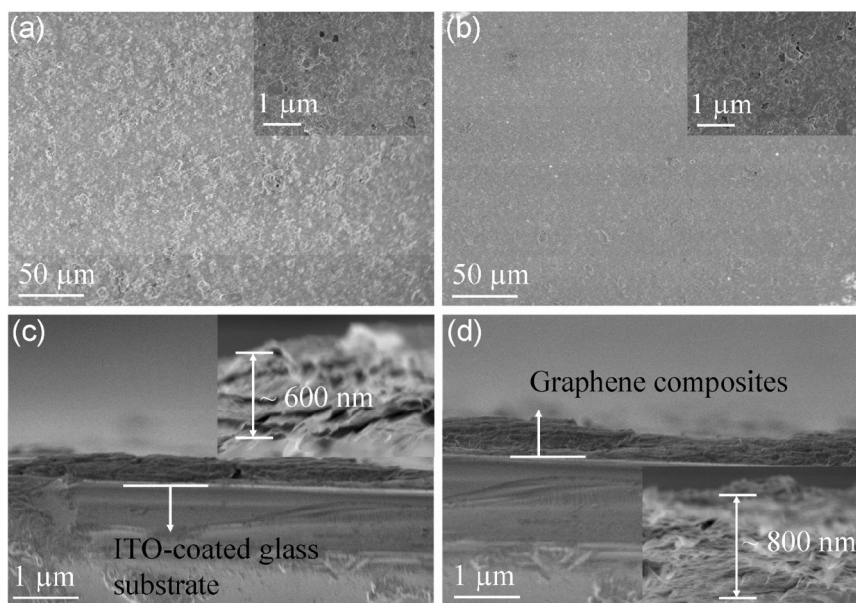


Fig. S9 Top-view SEM images of ZnP-GS (a) and RuP-GS (b), and side-view SEM images of ZnP-GS (c) and RuP-GS (d) deposited on ITO substrates. The insets are high magnification images.

Fig. S9 shows the SEM images of ZnP-GS and RuP-GS films spun casted on ITO substrates. The top-view images of ZnP-GS and RuP-GS films (Fig. S9 a, b) show that the films are continuous and very uniform. The films consist of large size graphene sheets with no evidence of aggregation. The side-view image of these films (Fig. S9 c, d) illustrate that the films consist of well-layered structure, and their thicknesses are ~ 600 and ~ 800 nm for ZnP-GS and RuP-GS films, respectively.

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