Electronic Supplementary Information (ESI)

A molecular approach to an electrocatalytic hydrogen evolution reaction on single-layer graphene

Sohyeon Seo,[a] Keunsik Lee,[a,b] Misook Min,[b] Yunhee Cho,[b] Meeree Kim,[b] and Hyoyoung Lee[a,b,c,d]*

[a]Centre for Integrated Nanostructure Physics (CINAP), Institute of Basic Science (IBS), 2066 Seoburo, Jangan-gu, Suwon 16419, Republic of Korea, [b]Department of Chemistry, [c]Department of Energy Science, and [d]SAINT, Sungkyunkwan University, 2066 Seoburo, Jangan-gu, Suwon 16419, Republic of Korea.

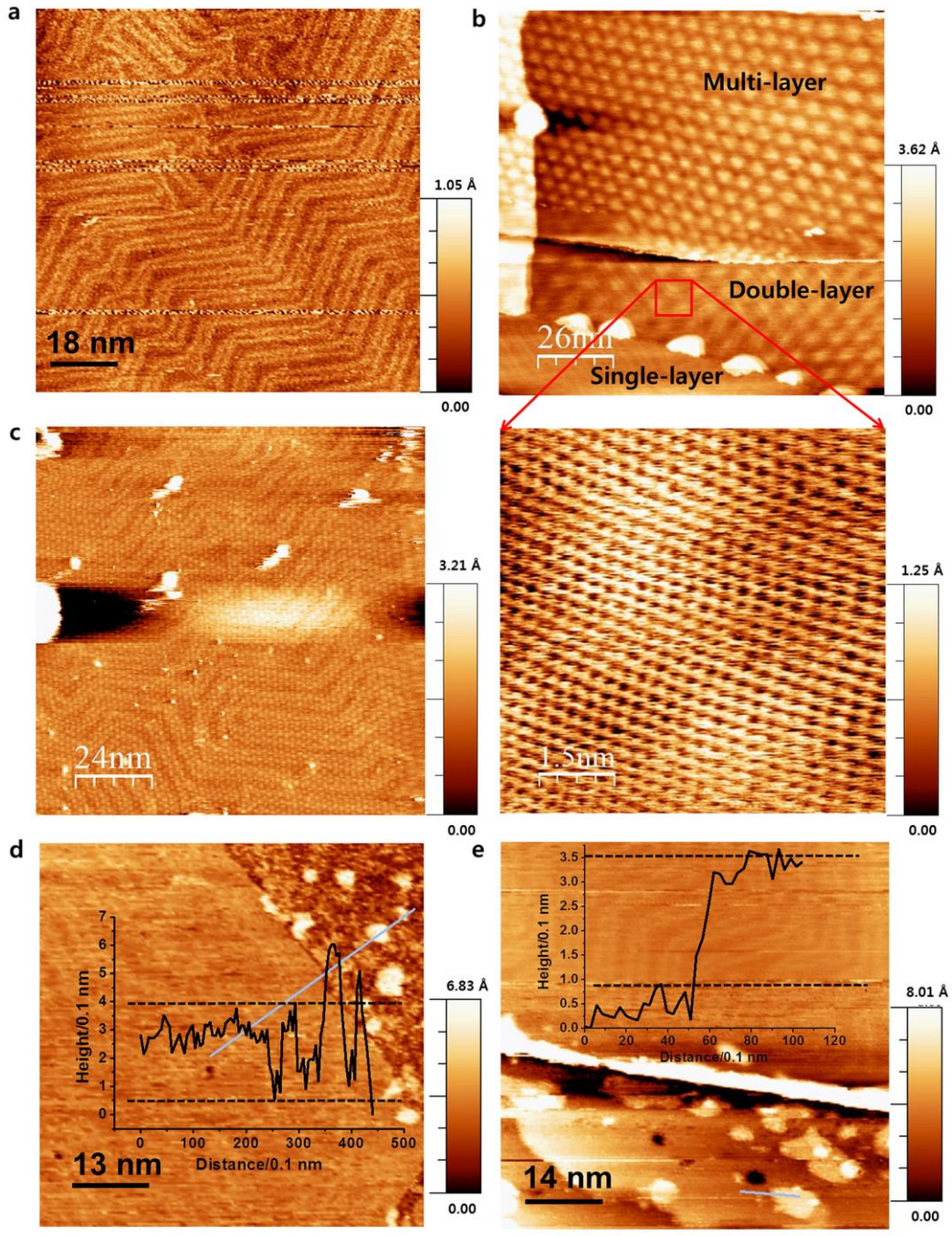

Fig. S1 Electrochemical scanning tunnelling microscopy (EC-STM) images**:** (a) Reconstructed bare Au(111) surface in 0.1 M H_2SO_4. (b) Multi-layered graphene on the reconstructed Au(111) surface in

0.1 M H_2SO_4. (c) Single-layered graphene on the reconstructed Au(111) surface in 0.1 M H_2SO_4 containing 0.05 mM 2H-TPyP molecules. (d) Zoomed-in image of Fig. 2d. (e) The graphene-covered and bare Au(111) surfaces after a pulse application of 0.65 V_{SCE}. Scanning conditions: a tunnelling current (I_t) of 0.1 nA, tip bias (V_{bias}) of 0.1 V, and sample potential of 0.0 V_{SCE}.

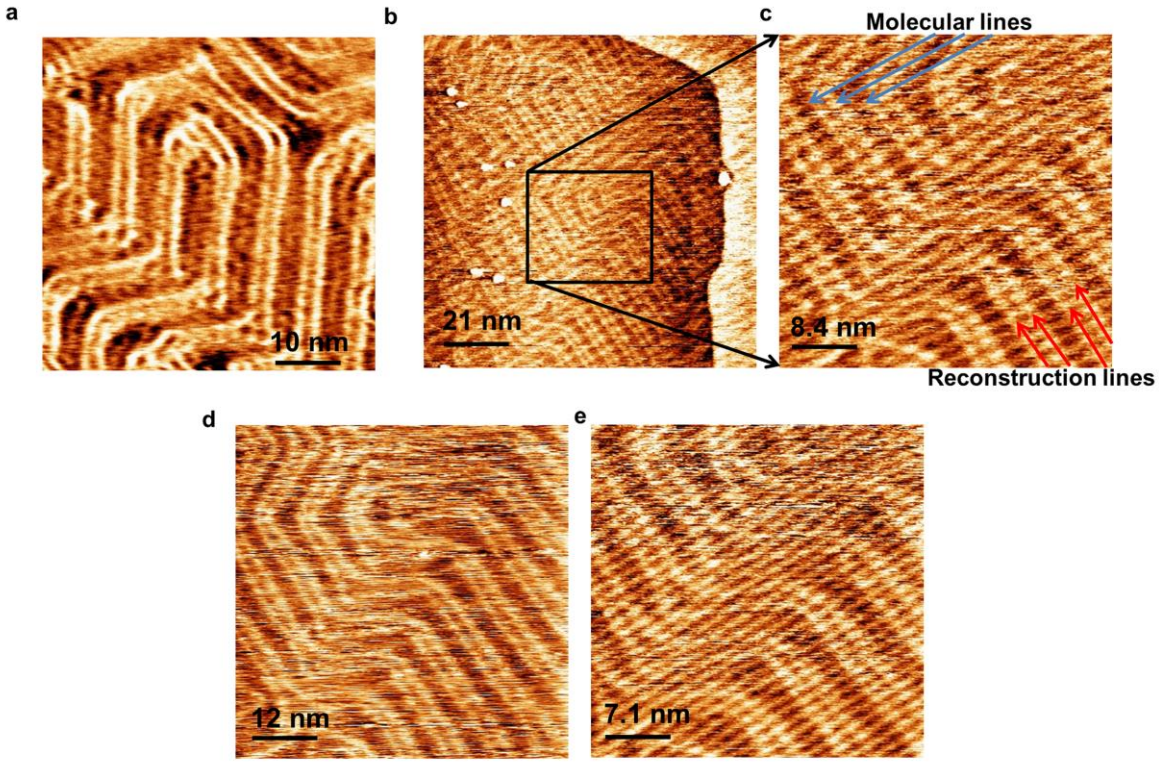

Fig. S2 Electrochemical scanning tunnelling microscopy (EC-STM) images**:** (a) Single-layered graphene on the reconstructed Au(111) surface in 0.1 M H_2SO_4 (a) without and (b)-(d) without 0.05 mM 2H-TPyP molecules. Scanning conditions with a tunnelling current (I_t) of 0.1 nA, tip bias (V_{bias}) of 0.1 V at sample potentials of (a), (b), (c), (e) 0.2 V_{SCE} and (d) 0.55 V_{SCE}. The images from (c) to (d) and (e) were obtained in a sequence.

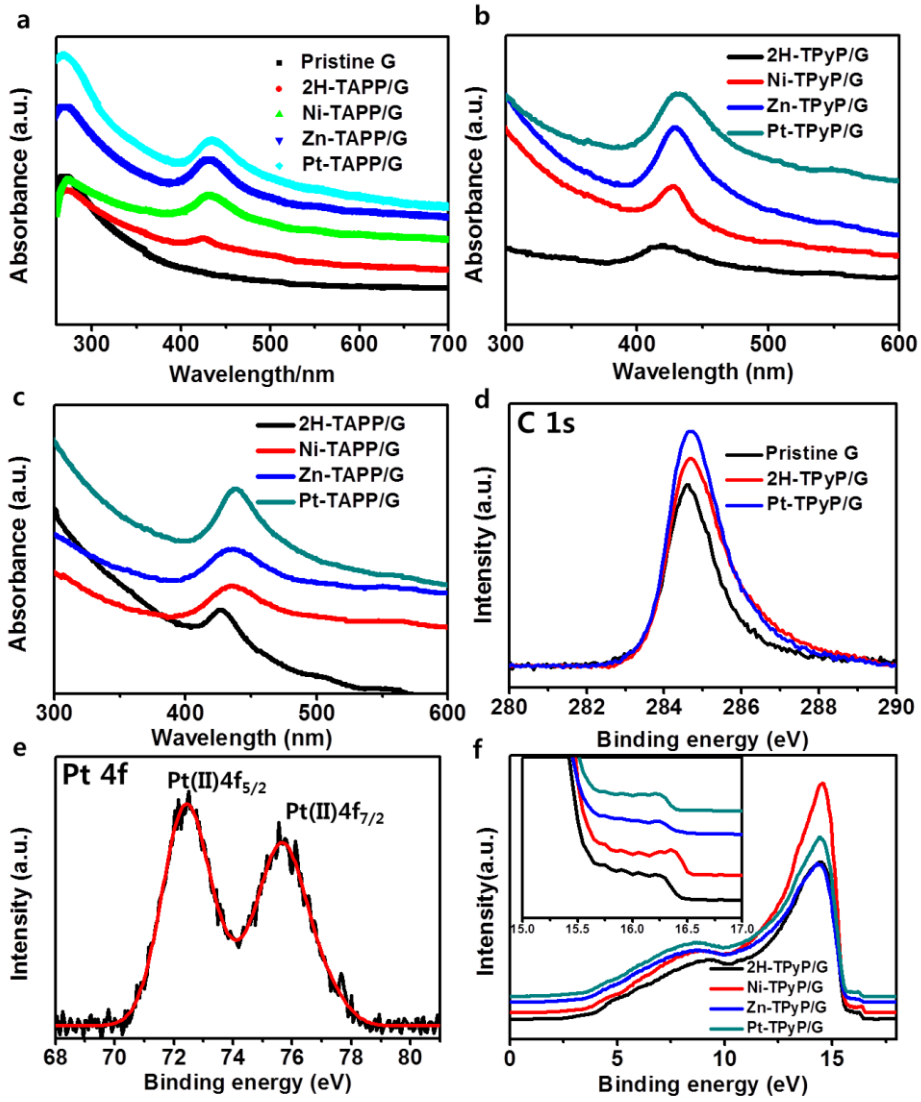

Fig. S3 Characterization of porphyrin adsorption and its metalation on graphene: (a)-(c) Changes in the UV-Vis spectra of graphene (G) as a function of surface modification with porphyrins (2H-TAPP, 2H-TPyP) and its metalation with Ni, Zn, and Pt by (a) thermal annealing and (b) (c) voltage application. (d) (e) XPS spectra of (d) C 1s for graphene (G), 2H-TPyP on graphene (2H-TPyP/G), Pt-TPyP on graphene (Pt-TPyP/G) and (e) Pt 4f for Pt-TPyP/G. (f) UPS spectra of 2H-TPyP/G and M-TPyP/G, M= Ni, Zn, and Pt.

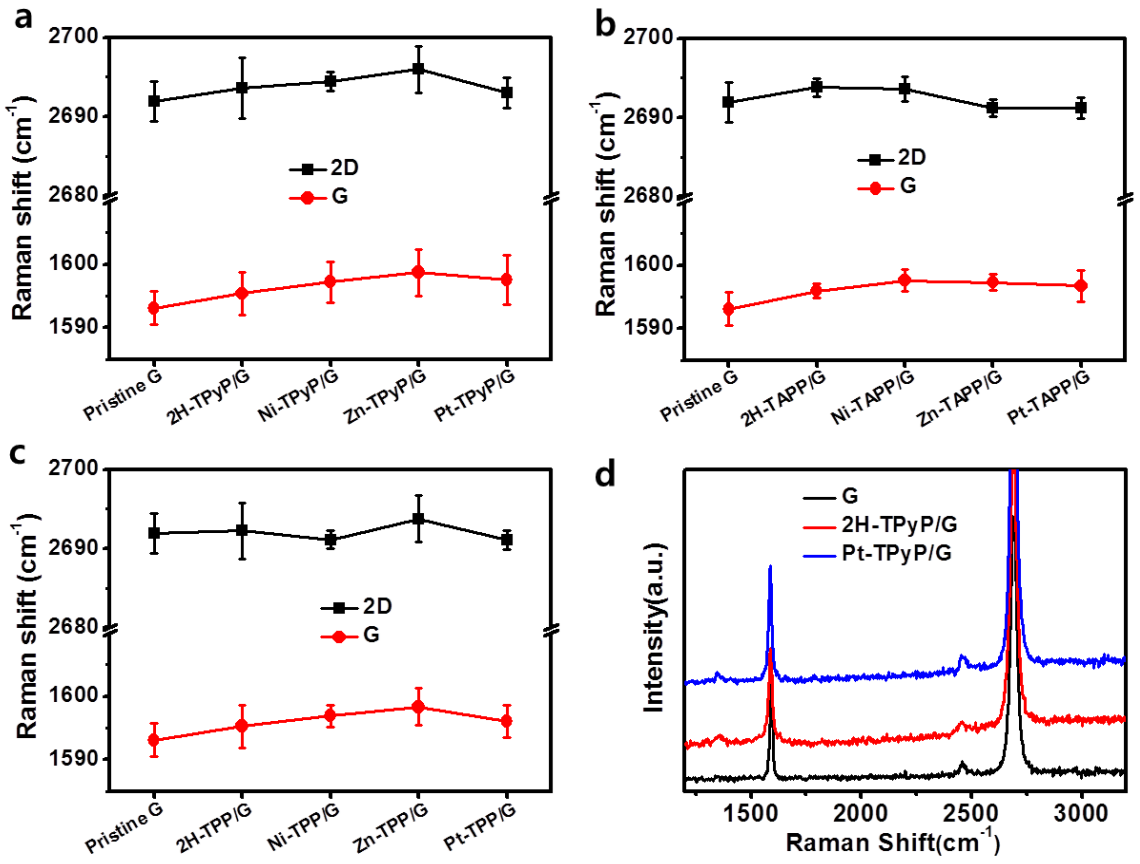

Fig. S4 Changes in Raman spectra: G and 2D peaks of graphene were evaluated with regard to adsorption of (a) 2H-TPyP and its metalation (M-TPyP, M = Ni, Zn, and Pt), (b) 2H-TAPP and its metalation (M-TAPP, M = Ni, Zn, and Pt), and (c) 2H-TPP and its metalation (M-TPP, M = Ni, Zn, and Pt). Metalation was accomplished by thermal annealing. Statistical analysis was conducted using 15 data points (standard deviation of 95%). (d) Raman spectra of pristine graphene, 2H-TPyP-adsorbed graphene, and Pt-metalized TPyP/graphene.

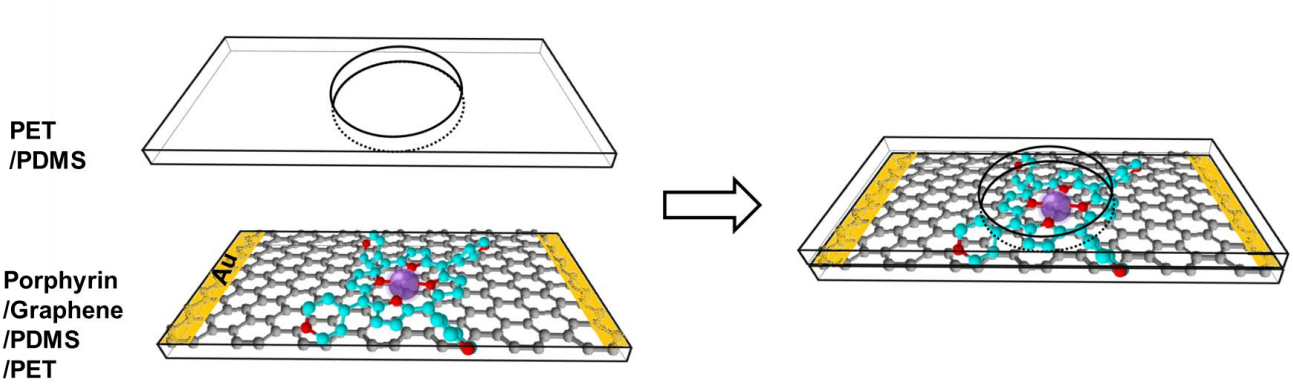

Fig. S5 Schematics of the graphene electrode used for electrochemical measurements: Metalation of porphyrin was accomplished by application of voltage between the two gold contacts. The top PDMS/PET substrate covered the bottom graphene electrode to enable determination of the electrode area.

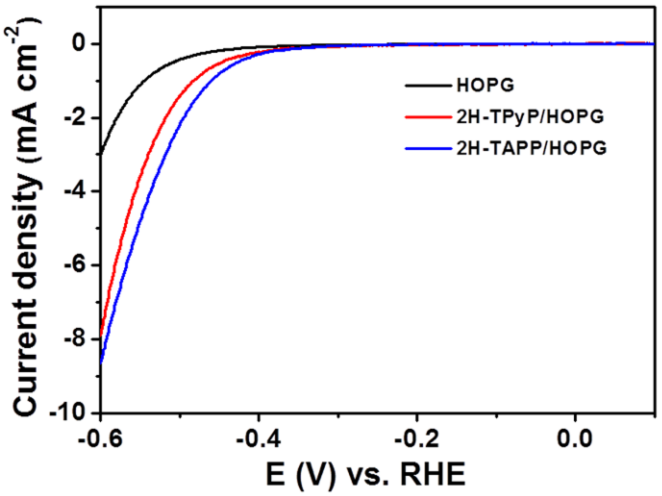

Fig. S6 Polarization curves of porphyrin-adsorbed HOPG for the hydrogen evolution reaction in 0.5 M H_2SO_4. HOPG substrate was fleshly prepared by tearing off the several top layers before immersion into porphyrin solution. Porphyrin-immobilized HOPG substrate was thoroughly washed with DI water several times and then dried for >24 h in a vacuum oven at 80 °C.

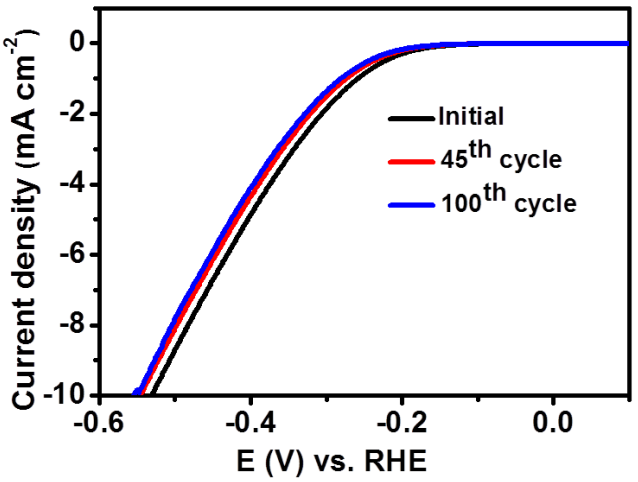

Fig. S7 Stability test for the Pt-TAPP/graphene electrode.

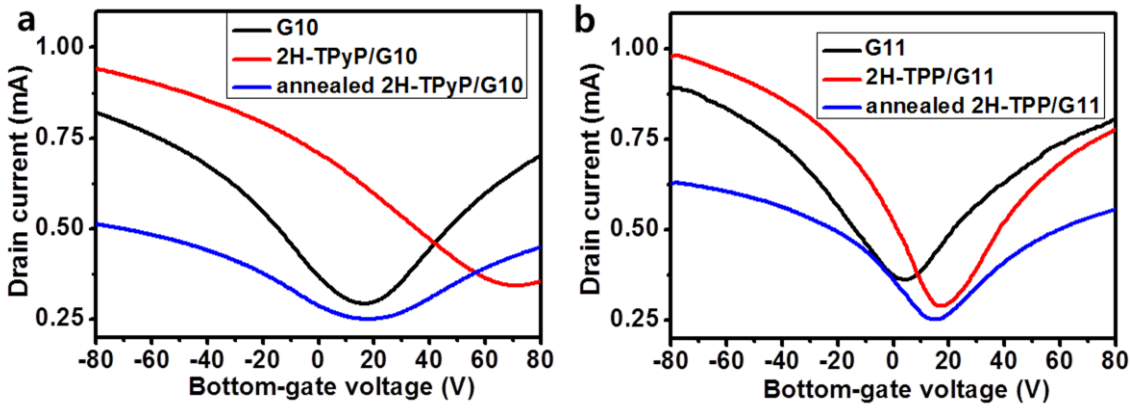

Fig. S8 Changes in transfer characteristics of graphene field effect transistors (FETs) in response to porphyrin adsorption and metalation on graphene: Effect of thermal annealing (at 250 °C) on (a) 2H-

TPyP/G and (b) 2H-TPP/G.

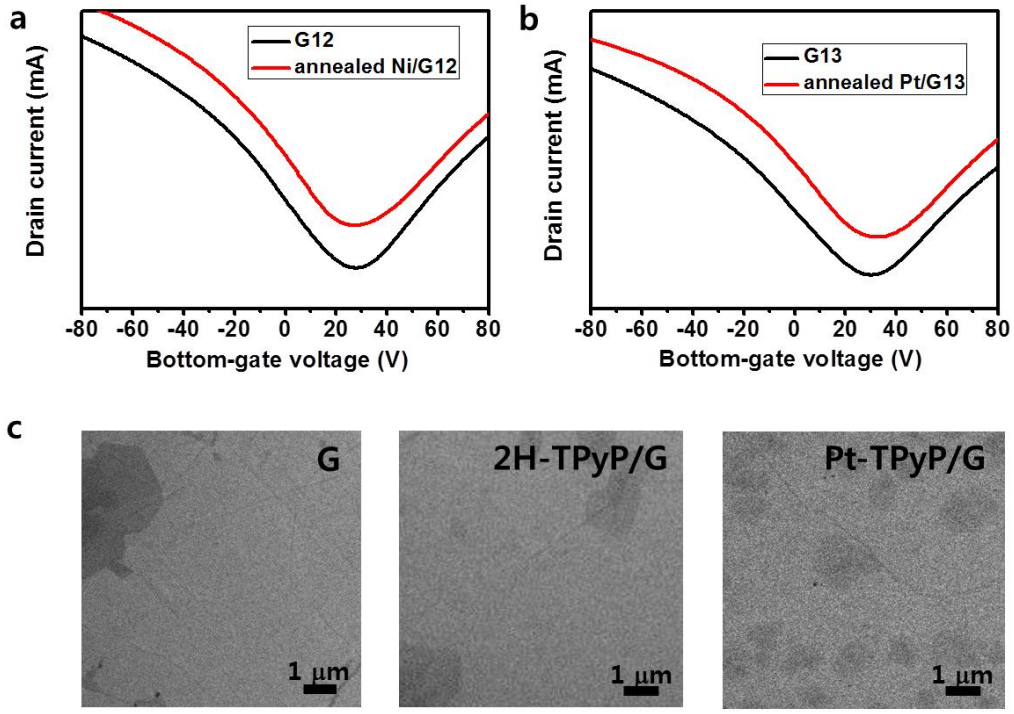

Fig. S9 Changes in transfer characteristics of graphene field effect transistors (FETs) in response to porphyrin adsorption and metalation on graphene: (a) (b) Effect of metal adsorption on graphene (without porphyrin) after immersion in (a) Ni^{2+} solution and (b) Pt^{2+} solution. (c) FE-SEM images of pristine graphene, 2H-TPyP-adsorbed graphene, and Pt-metalized TPyP/graphene.

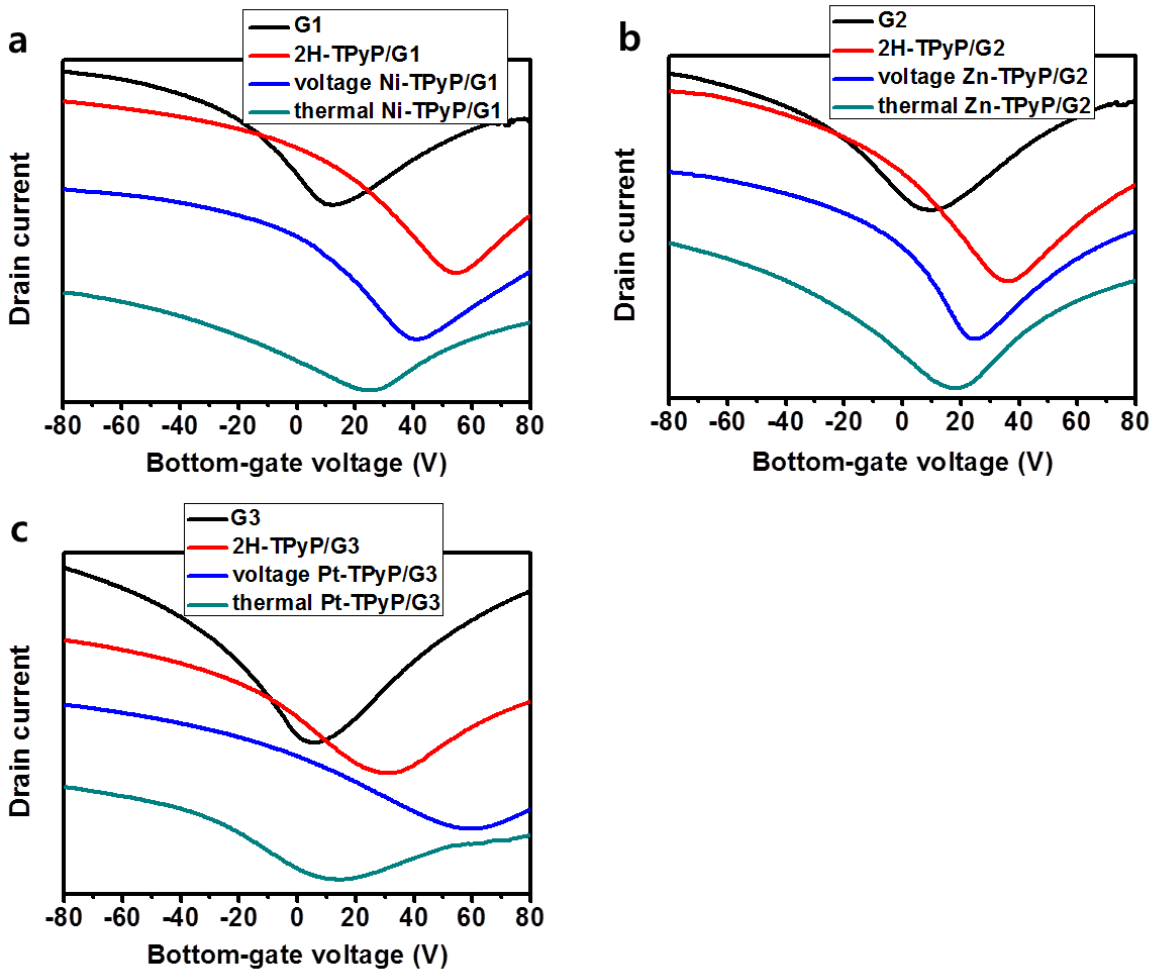

Fig. S10 Transfer characteristics of graphene FETs according to metalation**:** Changes in electronic properties of M-TPyP/G (M = (a) Ni, (b) Zn, and (c) Pt) treated by thermal annealing after metalation with voltage application.

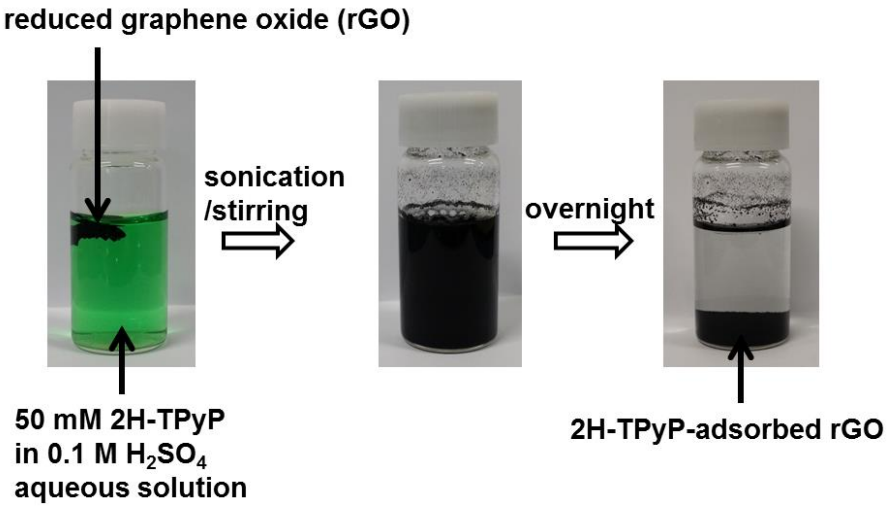

Fig. S11 Optical images of 2H-TPyP solution containing reduced graphene oxide (rGO) corresponding to adsorption of 2H-TPyP onto rGO.

Table S1. Binding energies (eV) in N 1s and metal XPS spectra of porphyrin and metalloporphyrin on graphene.

	N 1s (eV)		Metal	
	Pyrrolic N	Iminic N	Energy (eV)	Level
2H-TPP	400.9 ± 0.1	398.9 ± 0.1		
Ni-TPP	399.9 ± 0.1		855.1 ± 0.2	$2p_{3/2}$
Zn-TPP	399.8 ± 0.1		1022.6 ± 0.1	$2p_{3/2}$
Pt-TPP	399.4 ± 0.1		72.5 ± 0.1 75.6 ± 0.1	$4f_{7/2}$ $4f_{5/2}$
2H-TAPP	401.1 ± 0.2	398.5 ± 0.2		
Ni-TAPP	399.3 ± 0.1		856.9 ± 0.2	$2p_{3/2}$
Zn-TAPP	399.7 ± 0.1		1022.4 ± 0.3	$2p_{3/2}$
Pt-TAPP	399.8 ± 0.2		72.2 ± 0.2 75.6 ± 0.1	$4f_{7/2}$ $4f_{5/2}$
2H-TPyP	400.7 ± 0.3	398.6 ± 0.2		
Ni-TPyP	399.6 ± 0.2		857.3 ± 0.2	$2p_{3/2}$
Zn-TPyP	399.4 ± 0.1		1023.3 ± 0.3	$2p_{3/2}$
Pt-TPyP	399.6 ± 0.3		72.3 ± 0.1 75.6 ± 0.1	$4f_{7/2}$ $4f_{5/2}$

Table S2. Peak shifts of G and 2D in the Raman spectra of graphene in response to porphyrin adsorption and its metalation.

	2D (cm^{-1})	G (cm^{-1})
Pristine G	2691.9 ± 2.5	1593.1 ± 2.6
2H-TPP/G	2692.2 ± 3.6	1595.2 ± 3.3
Ni-TPP/G	2691.1 ± 1.1	1596.9 ± 1.7
Zn-TPP/G	2693.8 ± 2.9	1598.3 ± 2.9
Pt-TPP/G	2691.1 ± 1.2	1596.0 ± 2.5
2H-TAPP/G	2693.8 ± 1.1	1595.9 ± 1.1
Ni-TAPP/G	2693.6 ± 1.5	1597.6 ± 1.7
Zn-TAPP/G	2691.2 ± 1.0	1597.3 ± 1.3
Pt-TAPP/G	2691.2 ± 1.3	1596.7 ± 2.4
2H-TPyP/G	2693.6 ± 3.9	1595.4 ± 3.4
Ni-TPyP/G	2694.5 ± 1.2	1597.2 ± 3.2
Zn-TPyP/G	2694.0 ± 3.0	1598.7 ± 3.7
Pt-TPyP/G	2693.0 ± 1.9	1597.5 ± 4.0