Electronic Supplementary Information

Optical switching of Dirac point in graphene multilayer field-effect transistors functionalized with spiropyran

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Experimental

Synthesis of pyrene-modified spiropyran: Spiropyran was initially prepared by following a literature procedure (ref 25 in the manuscript; F. M. Raymo and S. Giordani, *J. Am. Chem. Soc.* 2001, **123**, 4651). Spiropyran (0.253 g, 0.72 mmol) was dissolved in dichloromethane (15.0 mL) after which *N,N'*-dicyclohexylcarbodiimide (0.221 g, 1.1 mmol), 4-dimethyl aminopyridine (8.74 mg, 0.07 mmol) and 1-pyrenebutyric acid (0.309 g, 1.1 mmol) were added over an ice bath. And then, the solution was stirred for 24 h at room temperature. The resulting white precipitate was filtered off and the filtrate was extracted with dichloromethane. The combined product mixture washed with aqueous $NaHCO_3$ and water and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography (Hexane/EtOAc = 5/1, R_f = 0.5). The product was obtained as a yellow solid (0.24 g, 53.6%). ^{1}H NMR (600 MHz, $CDCl_3$,): δ (ppm) = 7.78-8.28 (11H, m, ArH), 6.62-7.20 (6H, m, ArH), 5.76 (1H, d, *J*=10.2 Hz, ArH), 4.14-4.29 (2H, m), 3.30-3.49 (4H, m), 2.32-2.43 (2H, m), 2.10-2.19 (2H, m), 1.23 (3H, s), 1.09 (3H, s)

Preparation of graphene oxide (GO): Graphite oxide was synthesized from graphite powder (Bay Carbon SP-1 grade) by the modified Hummers method and exfoliated to give a brown dispersion of graphene oxide (GO) under ultrasonication. Briefly, graphite powders (1.0 g), $K_2S_2O_8$ (0.50 g) and P_2O_5 (0.50 g), were added to 3.0 mL of conc. H_2SO_4 with stirring until the reactants are completely dissolved. The mixture is kept at 80 ^oC for 4.5 h, after which the heating is stopped and the mixture diluted with 1.0 L of Millipore water. The mixture is filtered and washed to remove all traces of acid. For the oxidation step of the synthesis, the pretreated graphite is added to the 26 mL of H_2SO_4 and stirred. To this reaction mixture, 3.0 g of $KMnO_4$ was added slowly in an ice bath to ensure that the temperature remained below 10 ^oC. Then, this mixture reacts at 35 ^oC for 2 h after which 46 mL of distilled water is added under an ice bath. This mixture is stirred for 2 h at 35 ^oC, after which the heating is stopped and the mixture diluted with 140 mL of water and 2.5 mL of 30% H_2O_2 is added to the mixture resulting in a yellow color along with bubbling. The mixture is allowed to settle for at least a day after which the clear supernatant is decanted. The remaining mixture is filtered and washed with a 1.0 L of 10% HCl solution. The resulting solid is dried in air and diluted in distilled water that is put through dialysis for 2 weeks to remove any remaining materials and residues, after which the product was centrifuged and washed several times with Millipore water to neutralization and remove residual species. Finally, the dark brown GO powders were obtained through drying at 50 ^oC in a vacuum oven for a day. The GO powder dissolved in a known volume of water is subjected to ultrasonication for 30 min to give a stable suspension of GO (typically conc. 0.50 mg/mL) and then centrifuged at 4000 rpm for 10 min to remove any aggregates remained in the suspension.

Fabrication of the graphene FETs: The graphene multilayer FETs were fabricated onto a heavily doped n-type Si wafer with a thermally grown 300 nm-thick oxide layer (Si/SiO_2 wafer) that was pretreated with piranha solution. The Si wafer itself and the SiO_2 layer worked as the gate electrode and gate dielectric, respectively. After depositing the LbL-assembled multilayer graphene films, as described in detail in our previous report (ref 23 in the manuscript; H. Hwang, P. Joo, M. S. Kang, G. Ahn, J. T. Han, B. S. Kim and J. H. Cho, *ACS Nano* 2012, **6**, 2432.), the prepared graphene film was immersed in 1.0 mM ethyl acetate solution containing pyrene-modified with spiropyran (SP) for 24 h, followed by rinsing with ethyl acetate to remove any physisorbed SP molecules. Resulting samples were dried in a vacuum chamber for 12 h. Finally, Au source and drain electrodes were thermally deposited through a shadow mask. The channel length and width were 100 and 800 μm, respectively. The transistor current-voltage characteristics were measured at room temperature using Keithley 2400 and 236 source/measure units under vacuum (10^{-5} Torr). The surface coverage of pyrene functionalized spiropyran was estimated to be approximately 44% of the graphene multilayer electrode.

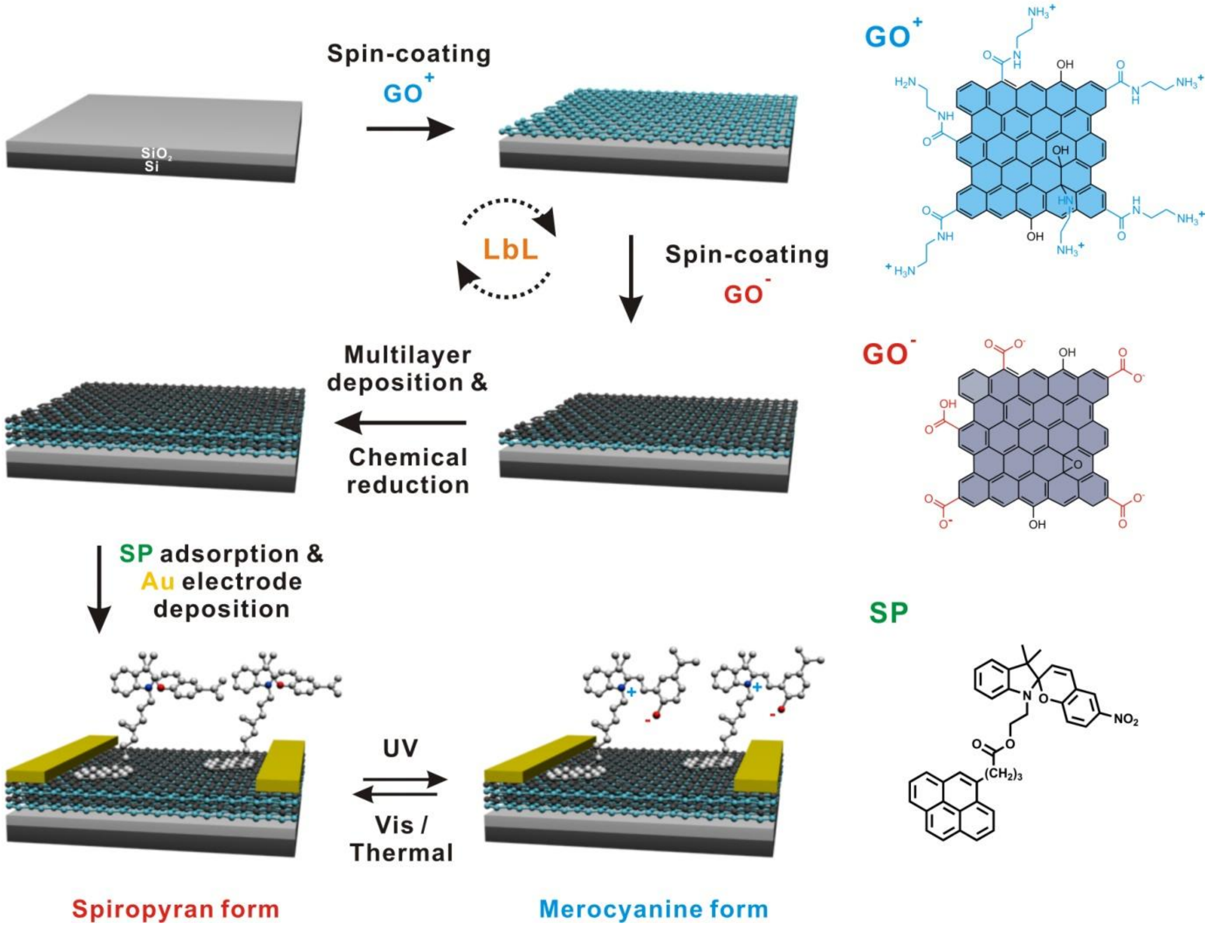

Fig. S1 (Left) Schematic representation of the photoresponsive spiropyran functionalized layer-by-layer (LbL) assembled graphene multilayer FET structures. (Right) chemical structures of positively and negatively charged graphene oxide nanosheets (GO^+ and GO^-) and pyrene-functionalized spiropyran (SP) used in this study.

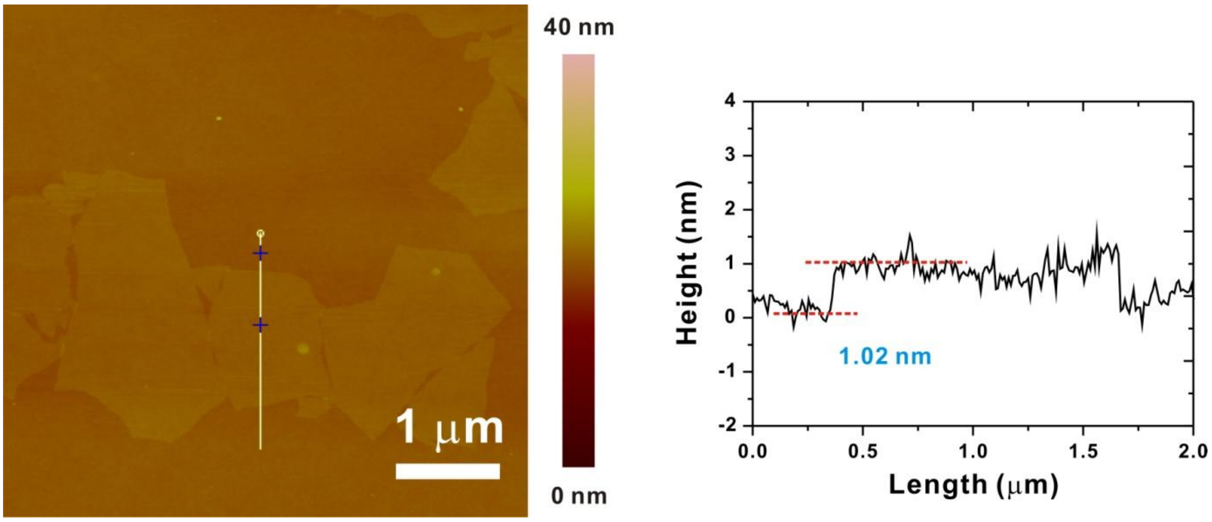

Fig. S2 Representative AFM image of graphene oxide (GO) nanosheet and the corresponding line scan profile.

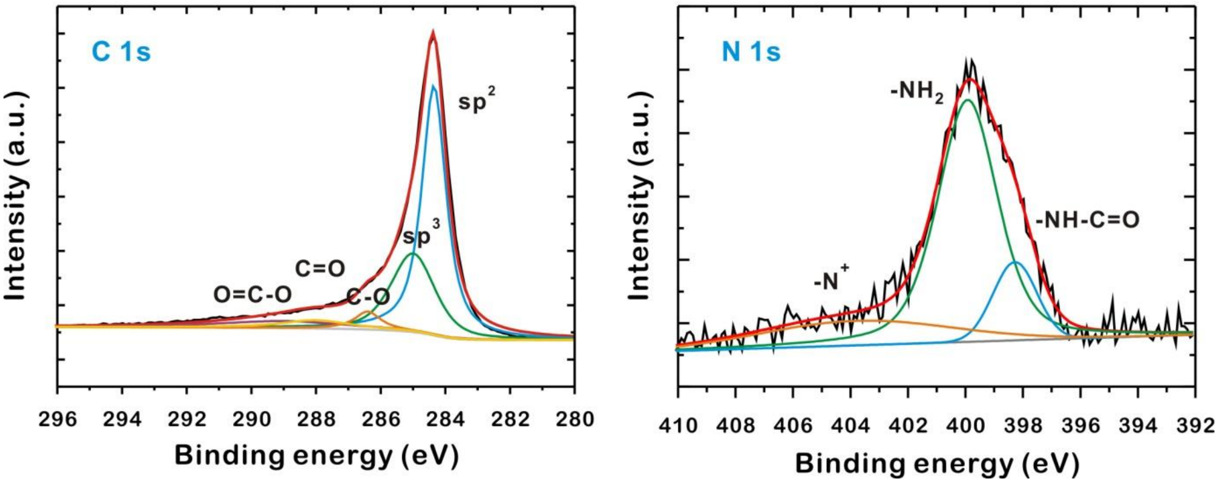

Fig. S3 High-resolution C 1s and N 1s XPS spectra of LbL-assembled 2-bilayer graphene multilayer.

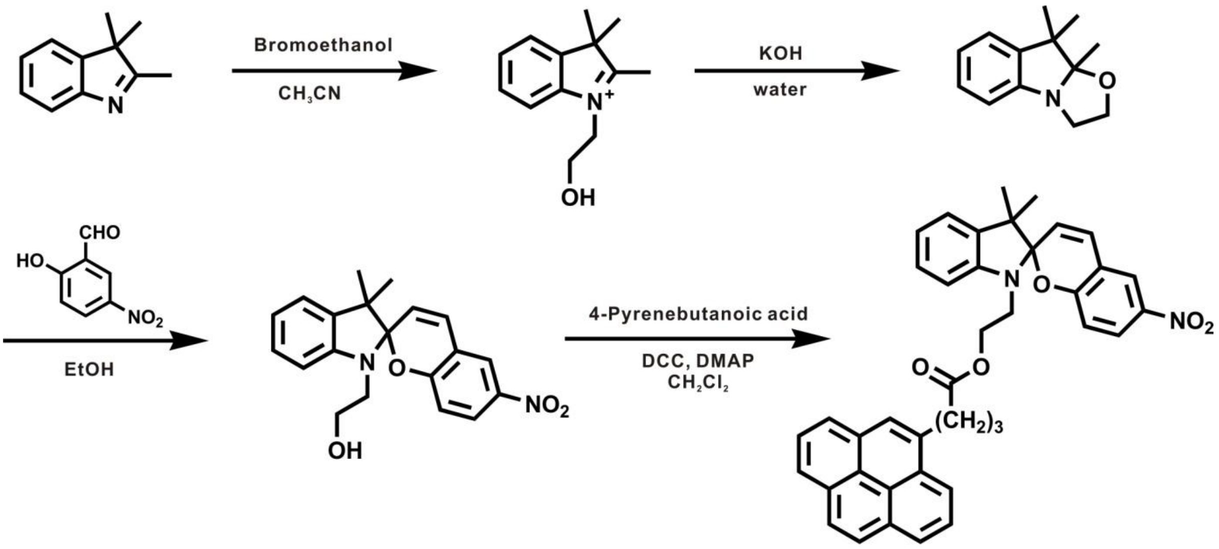

Fig. S4 Synthetic scheme for pyrene-functionalized spiropyran (SP) used in the study.

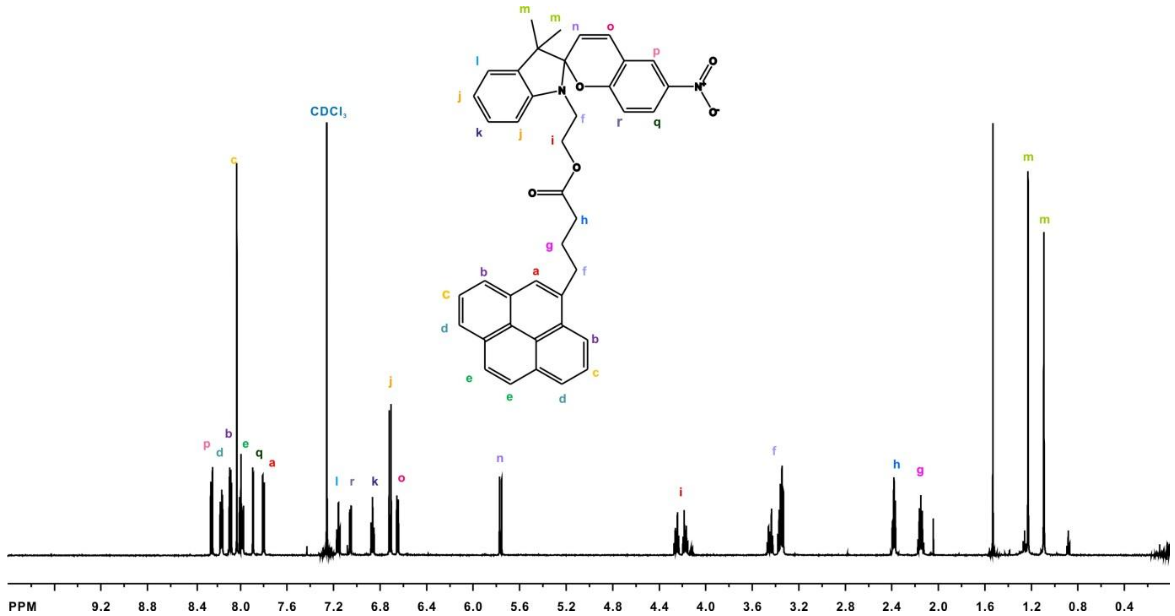

Fig. S5 ^{1}H-NMR spectrum of pyrene-functionalized spiropyran molecule (SP) (600 MHz, CDCl$_3$)

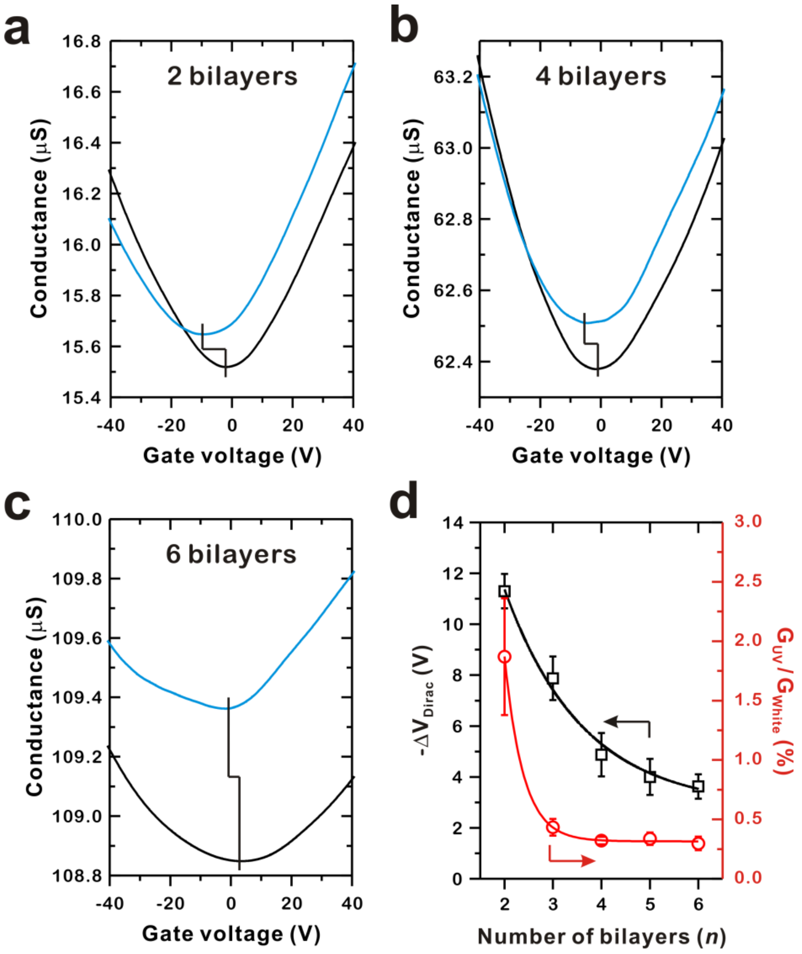

Fig. S6 (a-c) Transfer characteristics of the SP-functionalized 2, 4, and 6-bilayer graphene FETs (V_D = -0.1 V) (black) before and (blue) after UV irradiation for 5 min. (d) Dirac voltage shift ($-\Delta V_{Dirac}$) and minimum conductance ratio (G_{UV}/G_{white}) between UV and white light irradiation as a function of the number of bilayers. The lines in (a-c) are included to aid the Dirac voltage shift and conductance changes. All values were reported with three independent measurements.

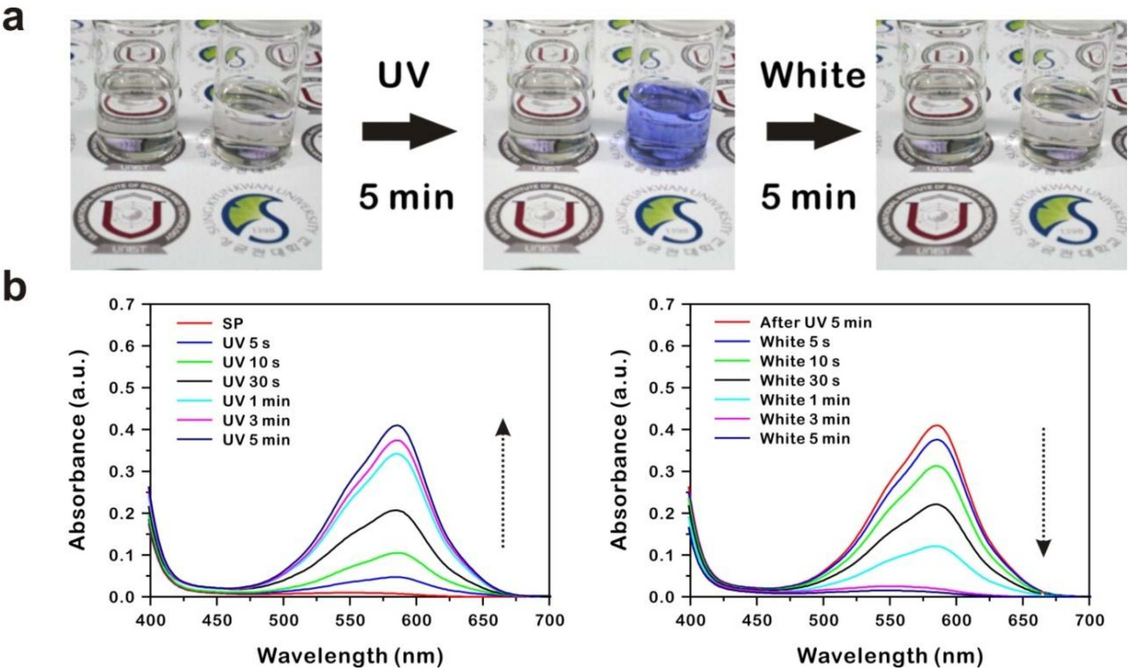

Fig. S7 Photoresponsive property of SP molecule. (a) (left) photograph of ethyl acetate solution and (right) SP in ethyl acetate solution under UV and white light illuminations. (b) Corresponding UV/vis spectra of SP under the identical light illuminations.

In order to investigate the kinetics of the photoswitching process of SP-functionalized graphene multilayer FETs, the I_D (at V_D of -0.1 V and V_G of 0 V) was monitored as a function of time (Fig. 3b in the manuscript). The channel conductance increased gradually with UV irradiation but decreased with white light irradiation. Interestingly, the rate of conductance variation was found to be different for UV and white light exposure. The obtained decay time constant for ring opening was 135.9 ± 2.0 s, whereas that for recyclization was 327.8 ± 5.9 s. These values are comparable with those in the previous results based on the SWNT devices with spiropyran molecules,[24] but apparently slower than that observed in solution (ca. 40 s). This difference may be due to the restricted motion of SP on the surface of graphene multilayers. In a clear contrast, control devices without SP modification did not exhibit any changes in conductance upon UV and visible light exposure, confirming the role of SP in the observed photoresponsive switching behavior (Fig. 3b in the manuscript).

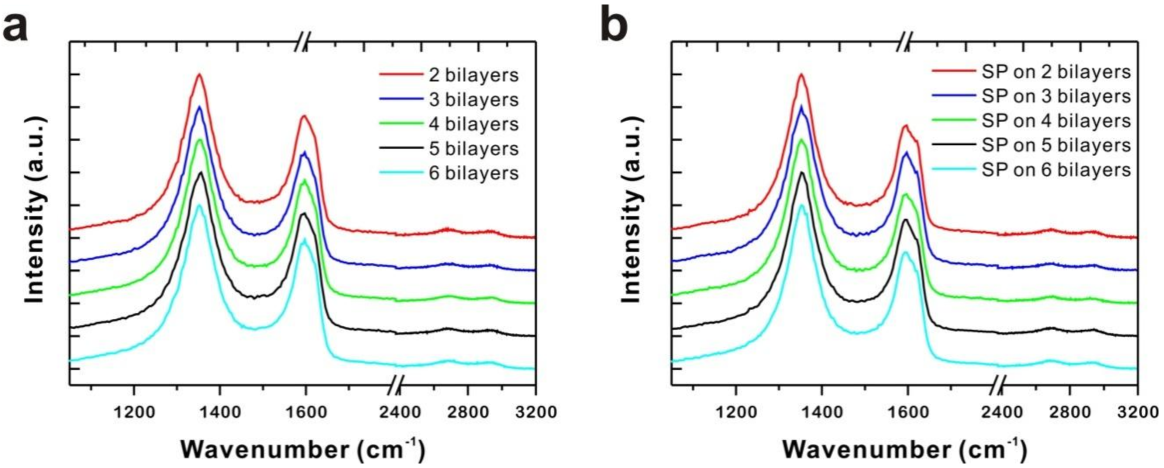

Fig. S8 Raman spectra of the LbL-assembled graphene multilayer films of different number of bilayers. (a) before and (b) after SP assembly. Two characteristic D-band (1352 cm^{-1}) and G-band (1597 cm^{-1}) observed from all samples did not shift upon UV and white light illuminations.

Raman spectroscopy is the most common and non-invasive technique to characterize the electronic structures of carbon materials. Representative Raman spectra showed two pronounced peaks, typically, D band at 1352 cm^{-1} and G band at 1597 cm^{-1} with a small 2D peak located at 2688 cm^{-1}, indicating a partial recovery of graphitic electronic structures. After the functionalization of SP and subsequent light illumination cycles, however, we could not monitor any shift nor intensity change in the D and G bands. Unlike the recent study by Gopalan group who observed a modest shift of G band upon functionalization with azobenzene moiety on pristine graphene (ca. 10 cm^{-1}) and light-induced shift (ca. 3 cm^{-1}), we speculate that our reduced graphene oxide based system which retains many defective sites limits the precise characterization of light-driven modulation of doping effect purely by Raman spectroscopy.