Electronic Supplementary Information (ESI) for:

Reduced Pyronin B as a Solution-Processable and Heating-Free *n*-Type Dopant for Soft Electronics

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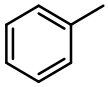
Table. S1 Summary of properties from the non-polar solvents (NPSs) tested in this study for the preparation of rPyB as an *n*-type dopant.

Non-polar solvent	Chemical structure	B.P.[a)] [°C]	Density [g mL^{-1}]	Dipole moment [*D*]
Pentane		36	0.626	0
Cyclopentane		40	0.751	0
Hexane		69	0.655	0
Cyclohexane		81	0.775	0
Benzene		80	0.875	0
Toluene		111	0.867	0.36

[a]Boiling point.

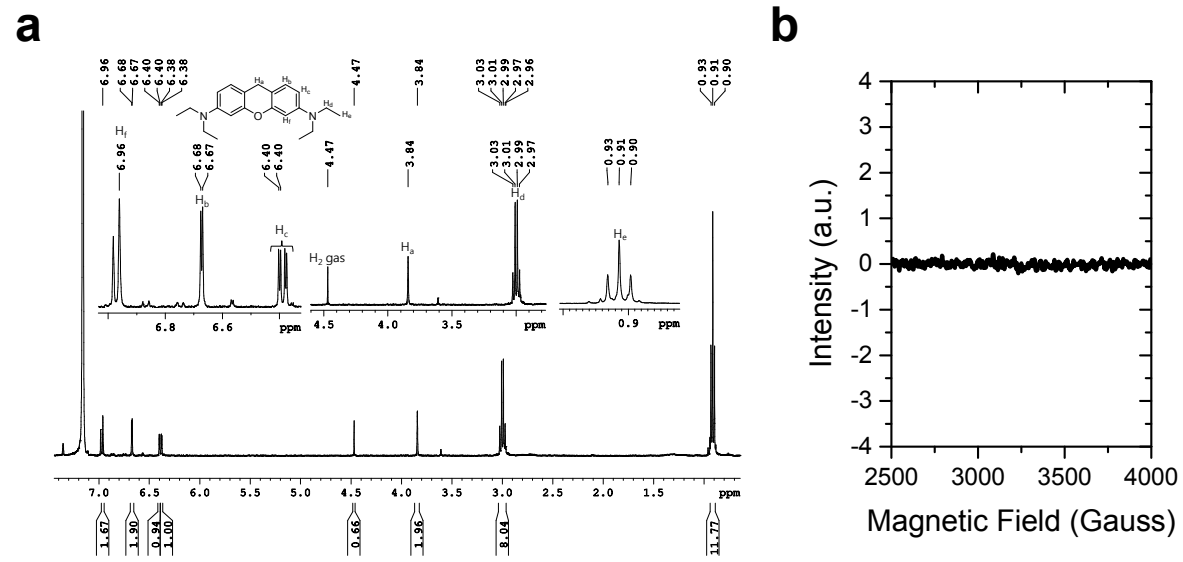


Fig. S1 (a) NMR Spectrum of rPyB: ^{1}H NMR (500 MHz, C_6D_6, 23 °C, δ): 6.96 (s, 2H), 6.68 (d, J = 5 Hz, 2H), 6.40 (d, J = 3.3 Hz, 1H), 6.38 (d, J = 3.3 Hz, 1H), 3.84 (s, 2H), 3.00 (q, J = 8.8 Hz, 8H), 0.91 (t, J = 7.0 Hz, 12H). (b) ESR spectrum of rPyB solution in hexane. Microwave frequency = 9.4508 GHz.

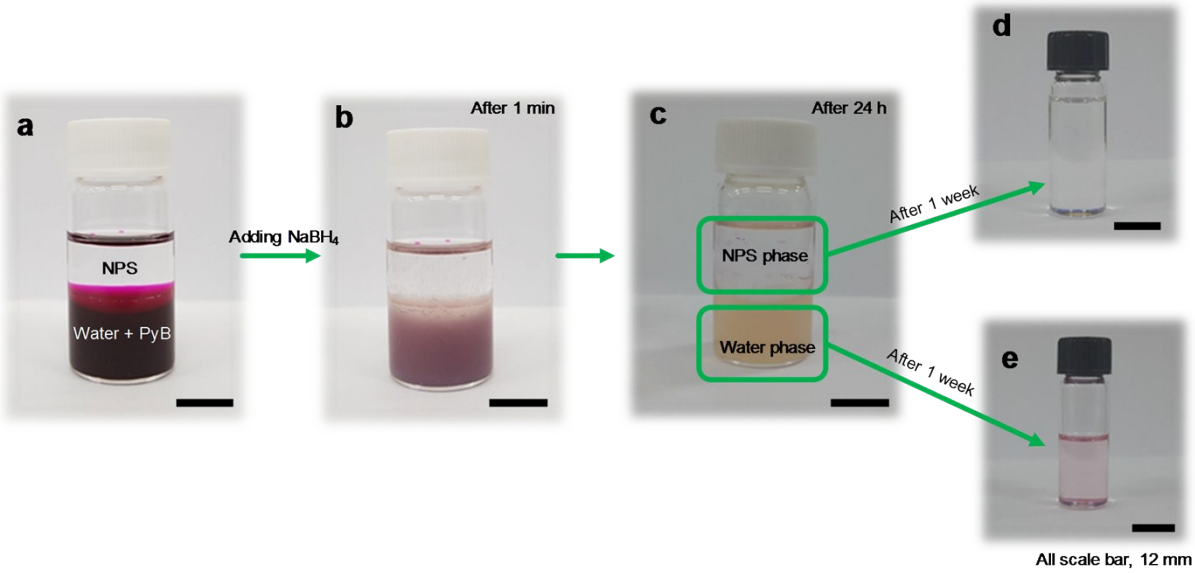


Fig. S2 Photographs of the biphasic solution reaction to synthesize rPyB. (a) A biphasic solution comprising NPS and water with PyB was prepared. Photographs (b) after 1 min of adding $NaBH_4$, and (c) after 1 day. The NPS and water part were separated. Photographs after 1 week of (d) NPS part containing rPyB and (e) water part.

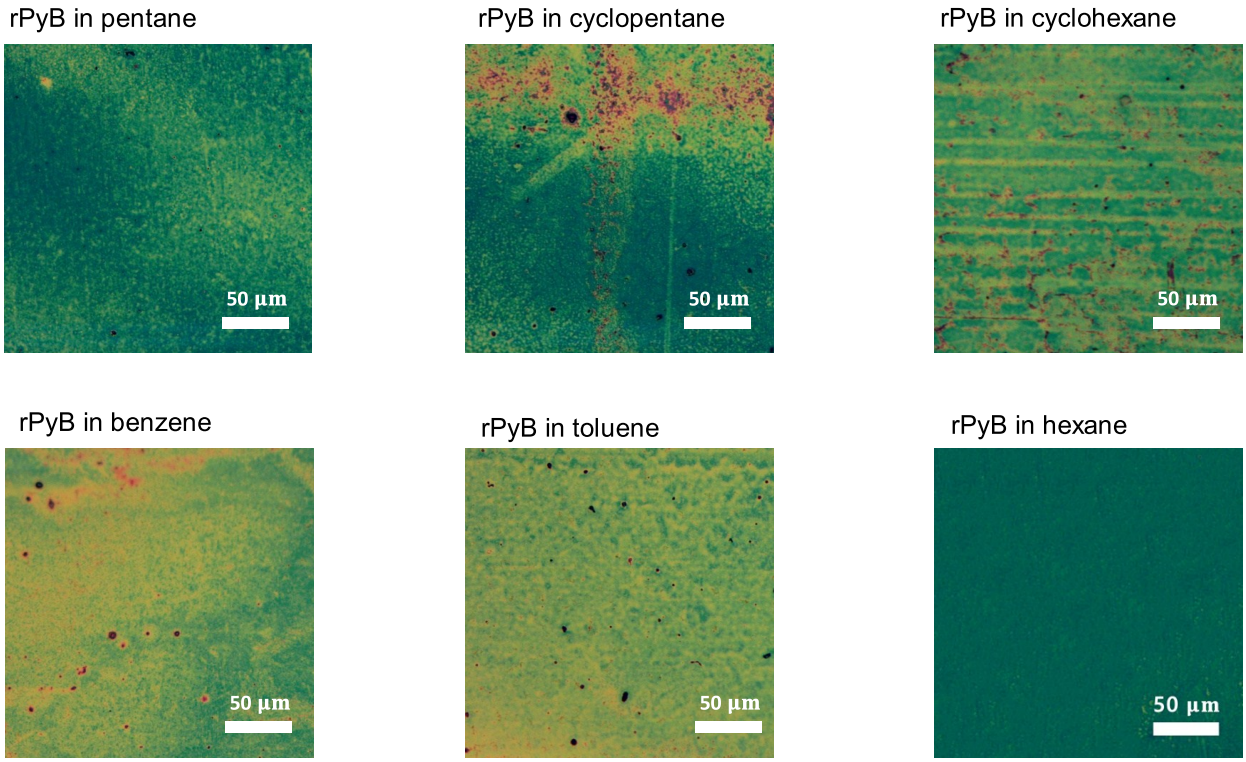


Fig. S3 Optical images of rPyB coated on graphene using various NPSs. All the rPyB solvents were spin-coated at 3000 rpm for 1 min. Evacuation at 1×10^{-3} torr was applied to remove NPSs for 10 min.

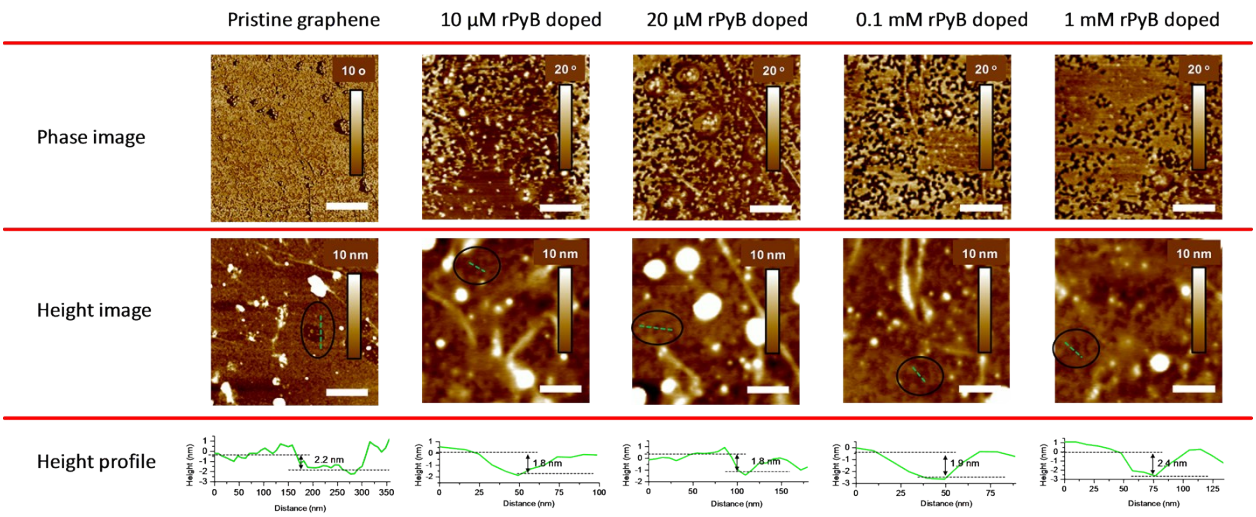


Fig. S4 AFM images (phase and height) of pristine graphene and rPyB-doped graphene with various doping concentrations (10 µM, 20 µM, 0.1 mM and 1 mM). From the phase images, rPyB coverages (brighter region) increased with increasing rPyB doping concentrations. Height profiles correspond to dashed green lines in each height images.

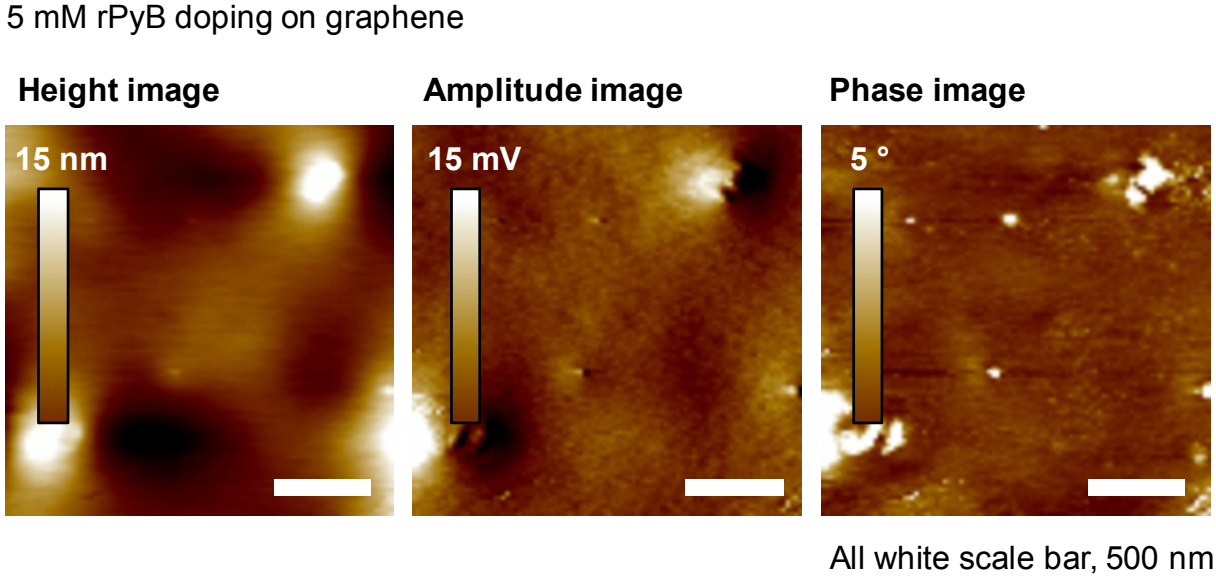


Fig. S5 AFM images of graphene film doped with 5 mM of rPyB solution.

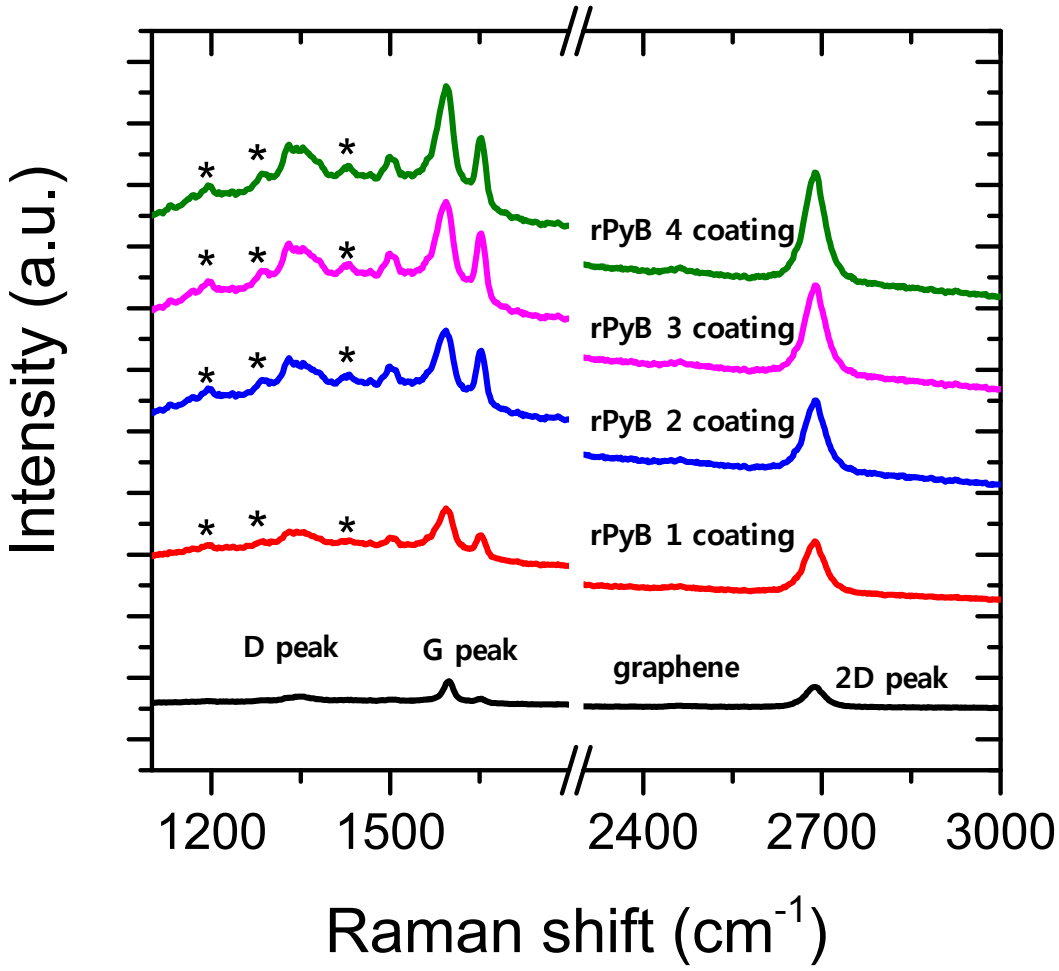


Fig. S6 Raman spectral changes of graphene as a function of the number of rPyB coating. Upon increasing the number of rPyB coatings, the corresponding Raman signal (marked with *) was enhanced, which can be attributed to graphene Raman enhanced signal. In addition, HMET can occur from rPyB to graphene, leading to an increased polarizability.

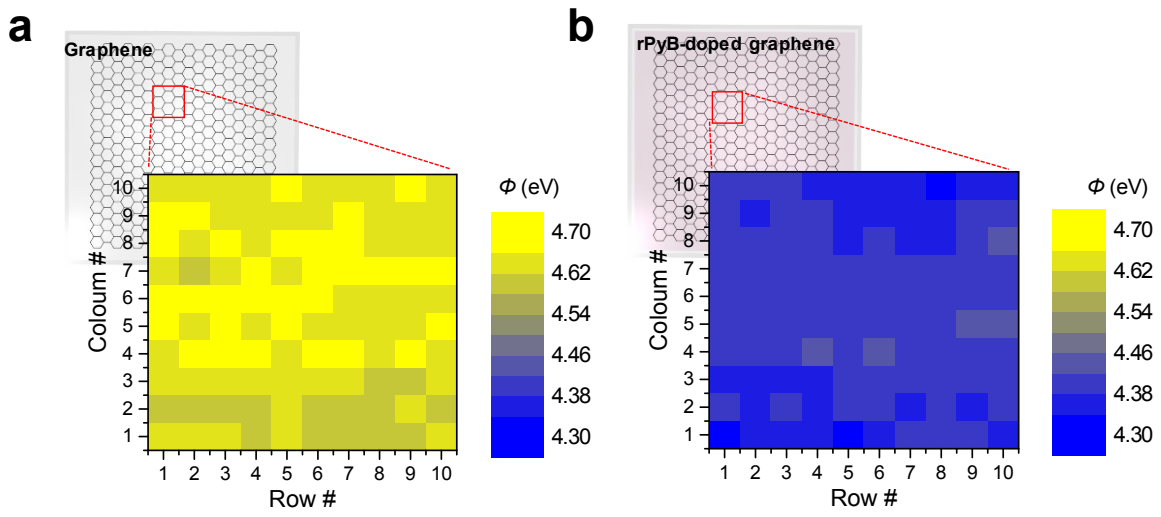


Fig. S7 Kelvin probe (KP) mapping (a) before and (b) after coating of rPyB on graphene.

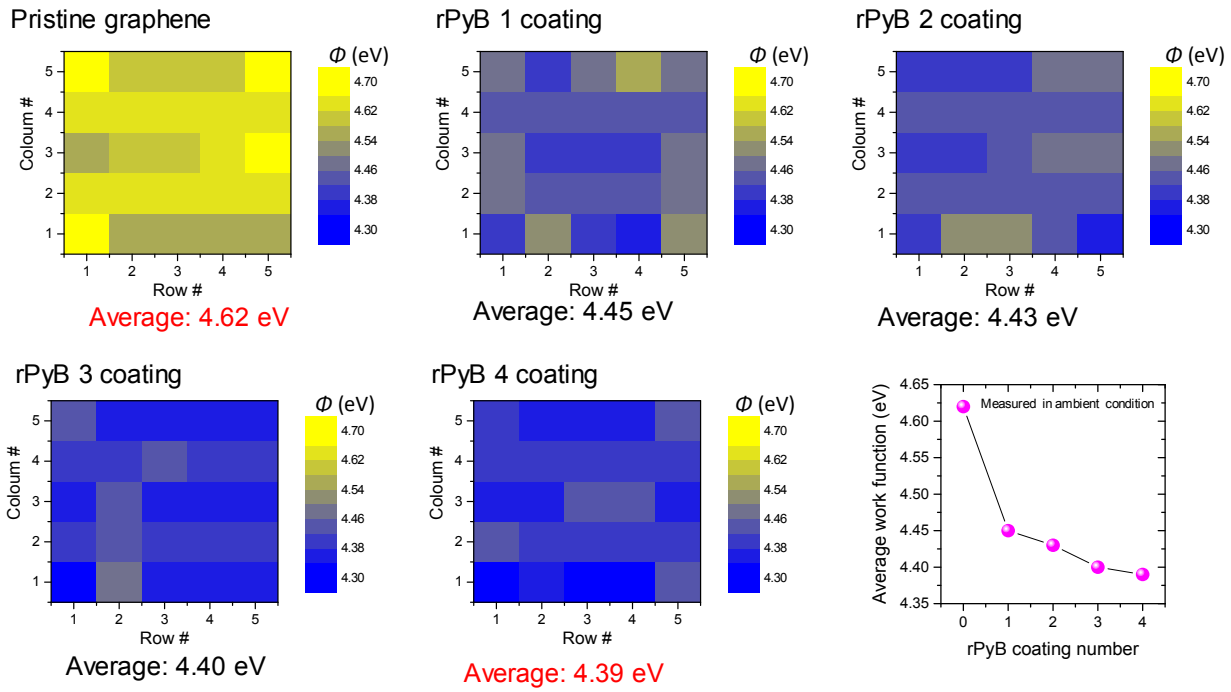


Fig. S8 Kelvin probe mapping of graphene with respect to the number of rPyB coating.

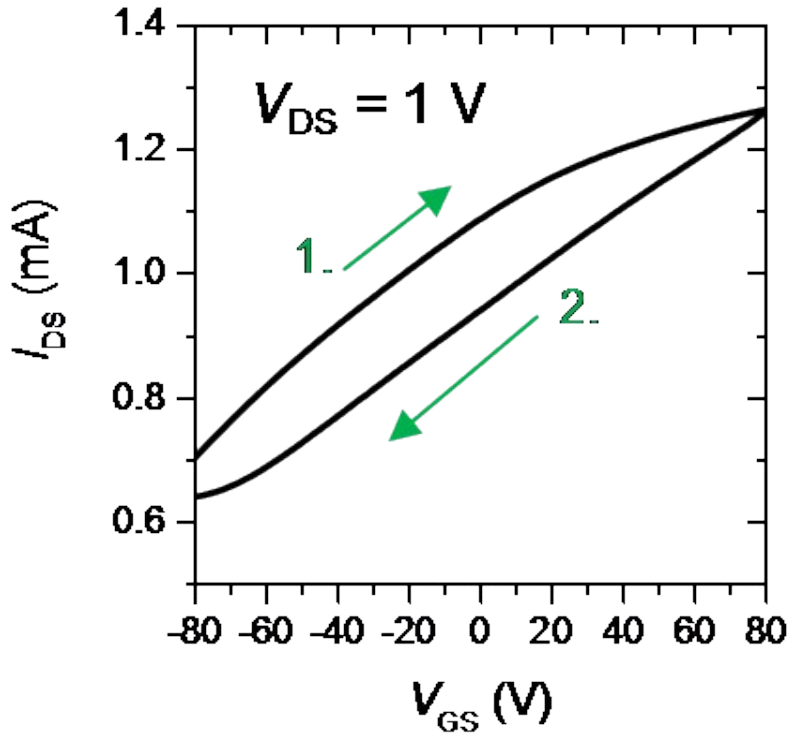


Fig. S9 The hysteresis of rPyB-doped graphene FET.

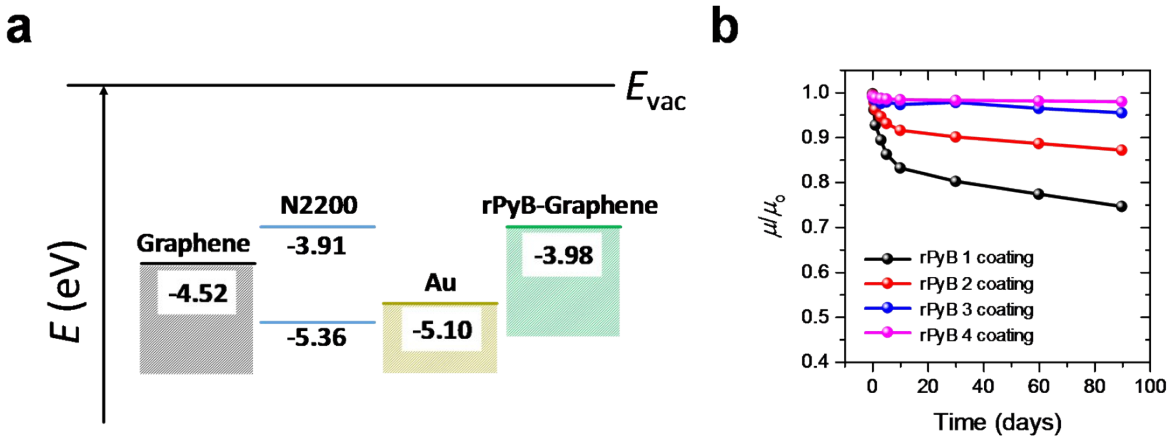


Fig. S10 (a) Comparison of energy levels of graphene, N2200, Au and rPyB-doped graphene. (b) Electron mobility changes of graphene FETs in ambient condition for 90 days as a function of the number of rPyB coating (from 1 to 4 rPyB coating).

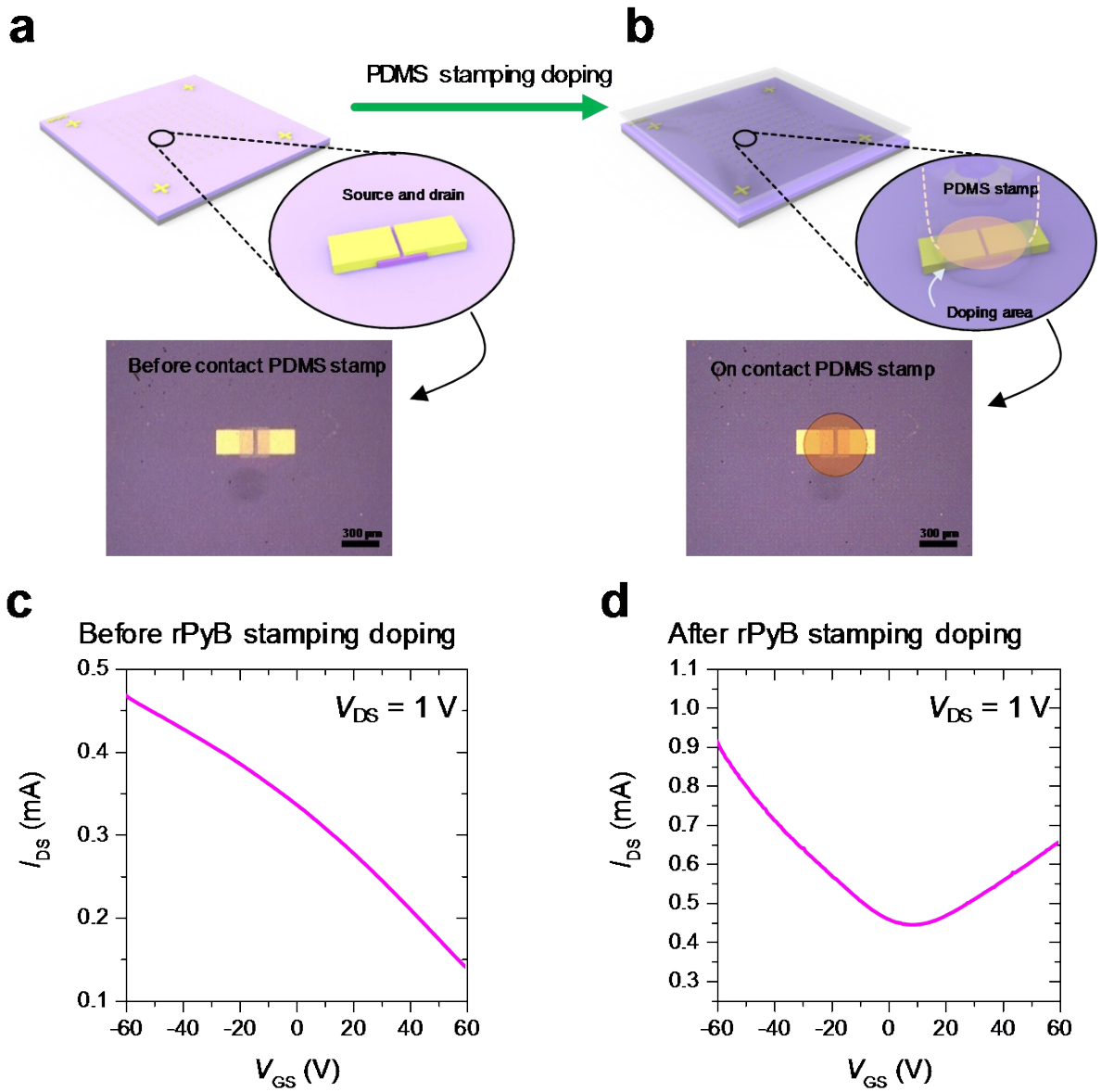


Fig. S11 Solution-processable, selective on-demand contact doping using a PDMS stamp. (a) 16 × 16 graphene FET array was fabricated on a 300 nm $SiO_2/n^{++}Si$ wafer using a conventional photolithography. (b) The fabricated PDMS stamp was soaked in rPyB solution. Then, the PDMS stamp dried under ~ 1×10^{-3} torr without thermal annealing was placed on top of the graphene FET array. Transfer curves of graphene FET (c) before and (d) after rPyB stamping doping.

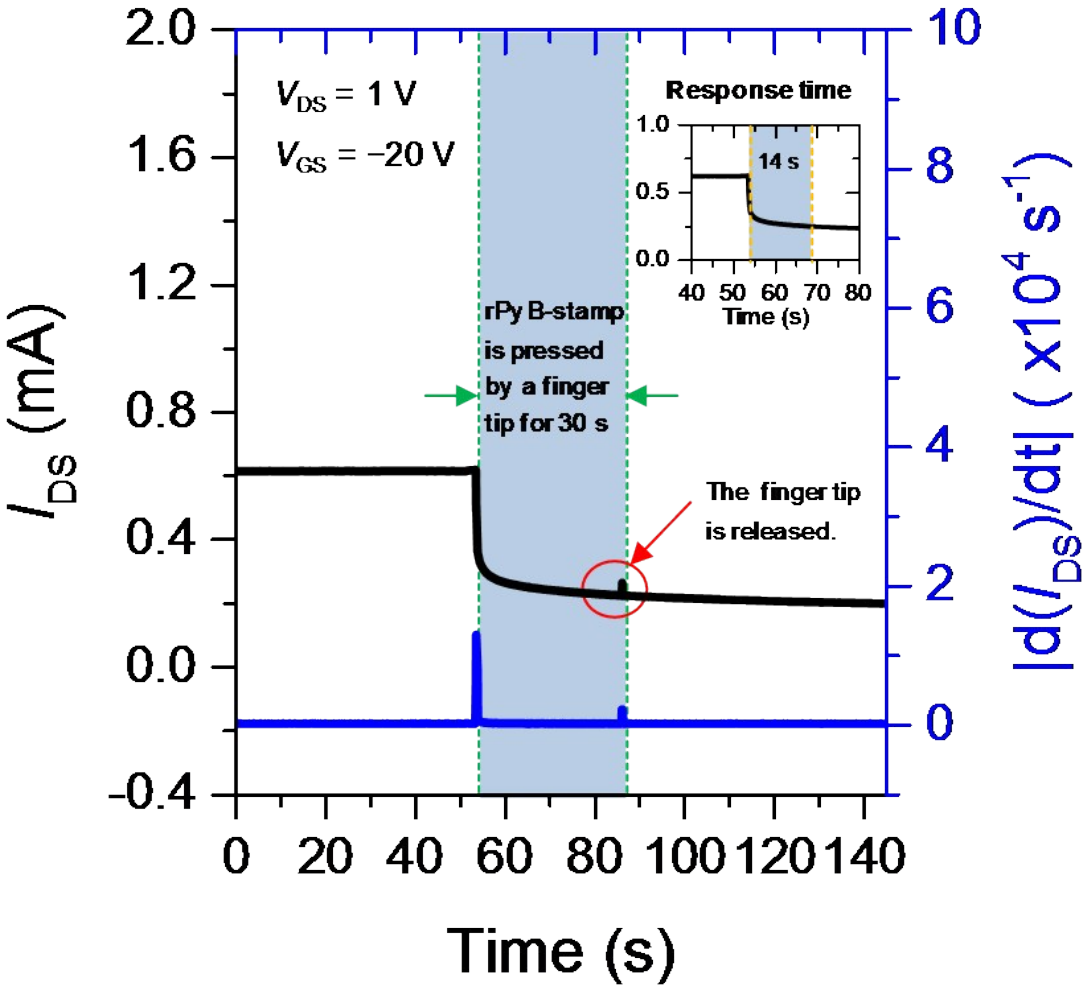


Fig. S12 The evaluation of response time for the rPyB-stamp doping effect on graphene FET. rPyB-stamp was pressed by a fingertip for 30 s. The obtained response time was 14 s. The inset is an enlarged plot with a timescale from 40 to 80 s. The response time was defined as the time required to reach the stable linear signal region after the rPyB-stamp doping.

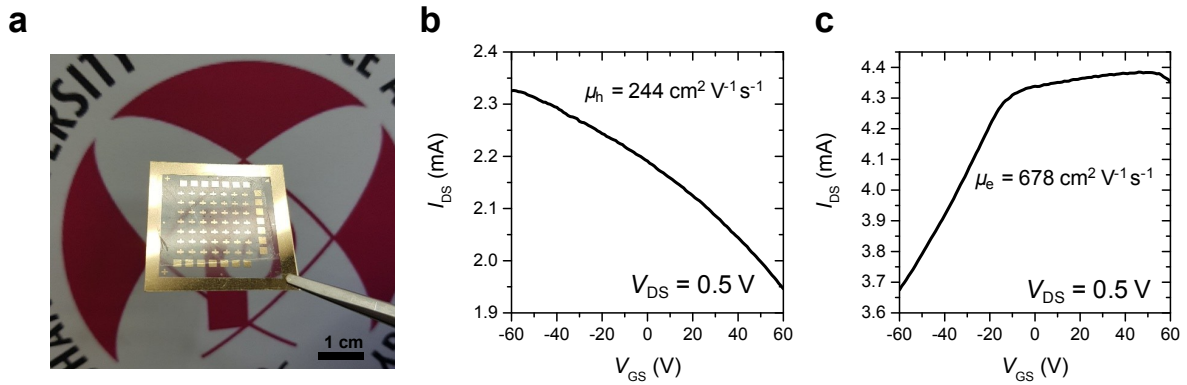
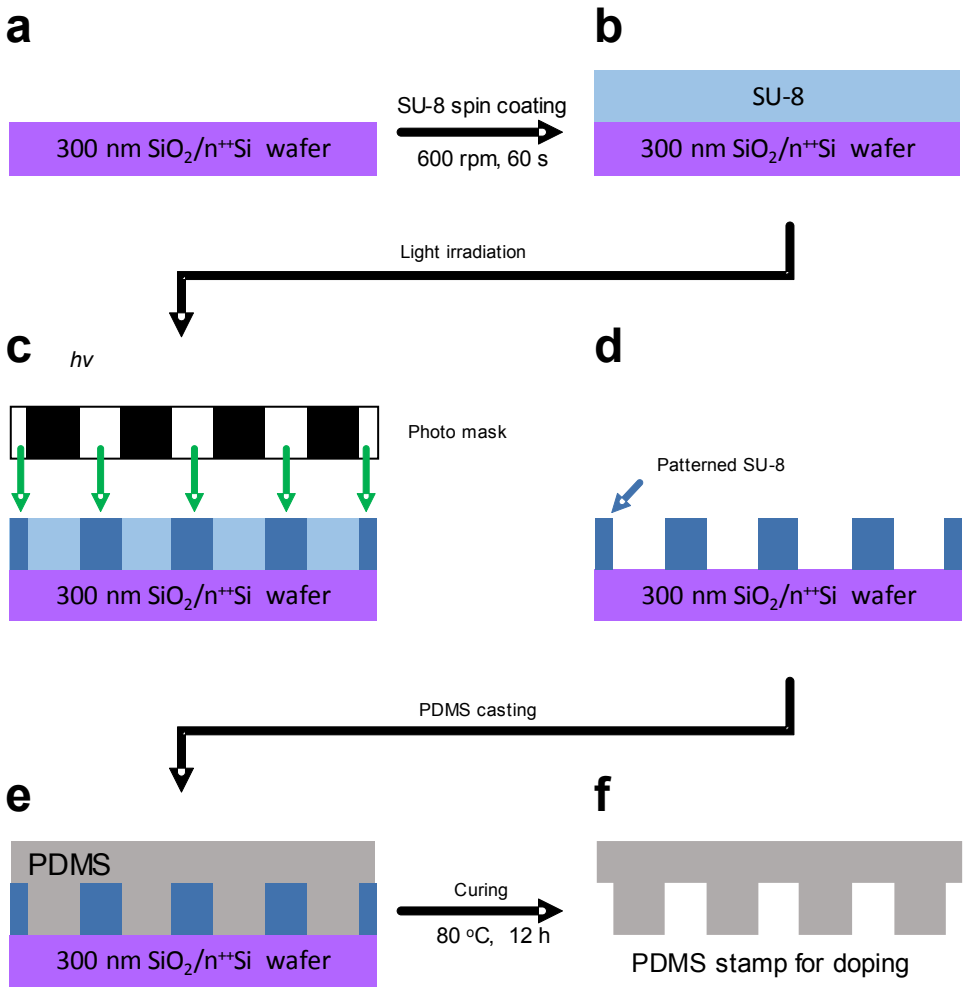


Fig. S13 (a) Photograph of rPyB-doped graphene FET array on a PET film. Morphological damages were not observed after the complete rPyB doping on the device. Typical transfer curve of graphene FET on PET (b) before and (c) after rPyB doping.

Appended Experimental Section

Fabrication of PDMS mold for 16 × 16 graphene FETs array stamping doping: To fabricate a PDMS stamp for the rPyB doping, (a) A washed Si wafer was prepared. (b) SU-8, a commercially available epoxy photoresist, was spin-coated on top of the Si wafer. (c) UV-light was irradiated through a photo mask to transfer the pattern of the stamp. (d) After the development of SU-8, (e) PDMS was cast on the patterned SU-8 mold. (f) Finally, the PDMS stamp was fabricated after curing at 80 °C for 12 h.



Schematic illustration of PDMS stamp and the detail for the preparation of stamping doping: The fabricated PDMS stamp was 16 × 16 bumps with 500 μm, 20 μm of diameter and height, respectively and the distance between bumps is 1.5 mm. The fabricated PDMS stamp was soaked into rPyB solution for 1 min. After drying toluene at 120 °C, PDMS stamp was placed on the position of destination.