

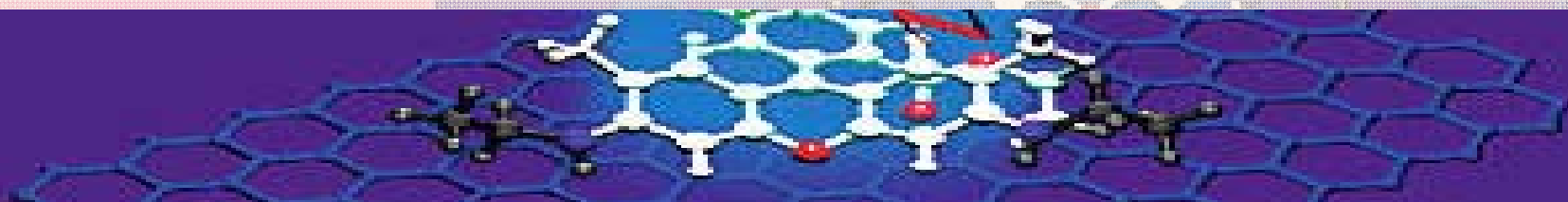
Graphene as a Substrate to Suppress Fluorescence in Resonance Raman Spectroscopy

Liming Xie, Xi Ling, Yuan Fang, Jin Zhang, and Zhongfan Liu

J|A|C|S
COMMUNICATIONS

ASAP Article ; Published on July 2, 2009, doi: 10.1021/ja9037593

Beijing National Laboratory for Molecular Sciences, Key Laboratory for the Physics and Chemistry of Nanodevices, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing, P. R. China

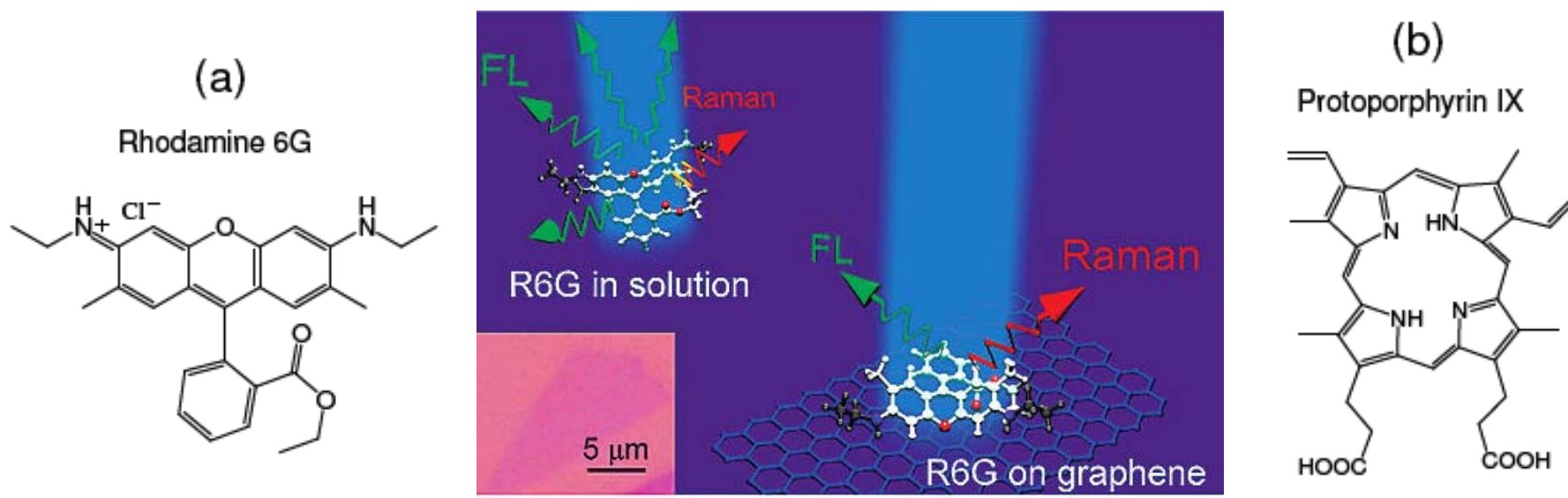


Introduction

- Resonance Raman spectroscopy (RRS) is a powerful approach to characterize structures of chemicals at low concentrations.
- Vibrational frequencies of the analyte molecules are in resonance with the incident frequency.
- RRS can enhance Raman signal by 10^7 times than normal Raman spectroscopy.
- Fluorescence (FL) background is a major obstacle in RRS because the FL cross section is much larger than the RRS cross section.
- Several approaches, such as ultraviolet RRS (UV-RRS), time-resolved Raman detection, femtosecond broadband stimulated Raman spectroscopy (FSRS), and coherent anti-Stokes Raman spectroscopy (CARS), have been used to suppress or reject FL background in RRS.

About the paper

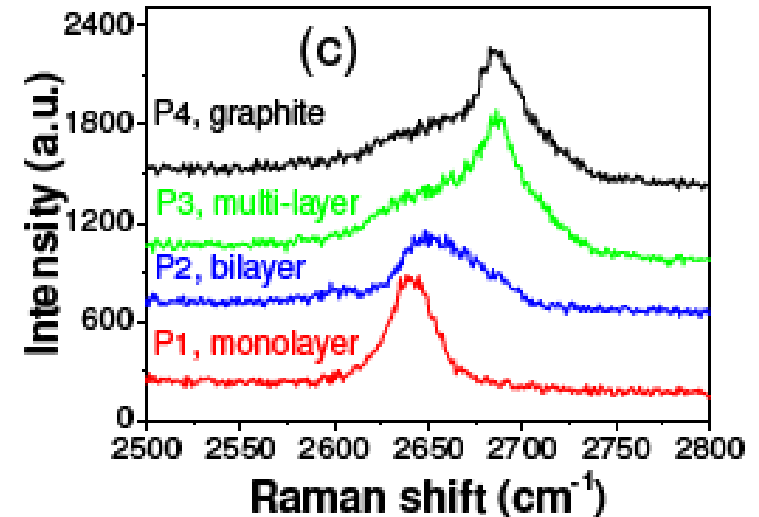
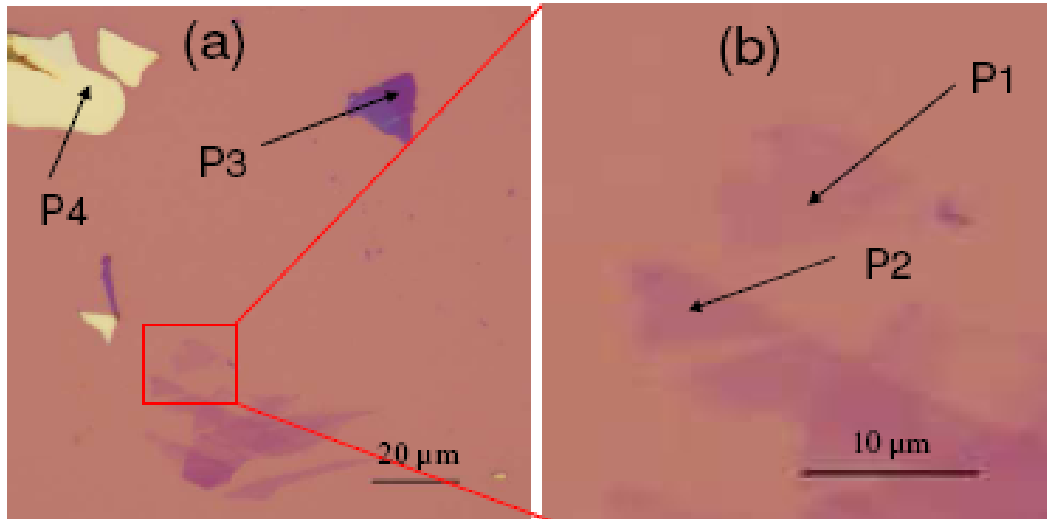
- Graphene can be used as a substrate to suppress FL background by $\sim 10^3$ times which can be used to measure RRS from fluorescent molecules at low concentrations.
- Two probe molecules were used in this work: Rhodamine 6G (R6G) and Protoporphyrin IX (PPP).



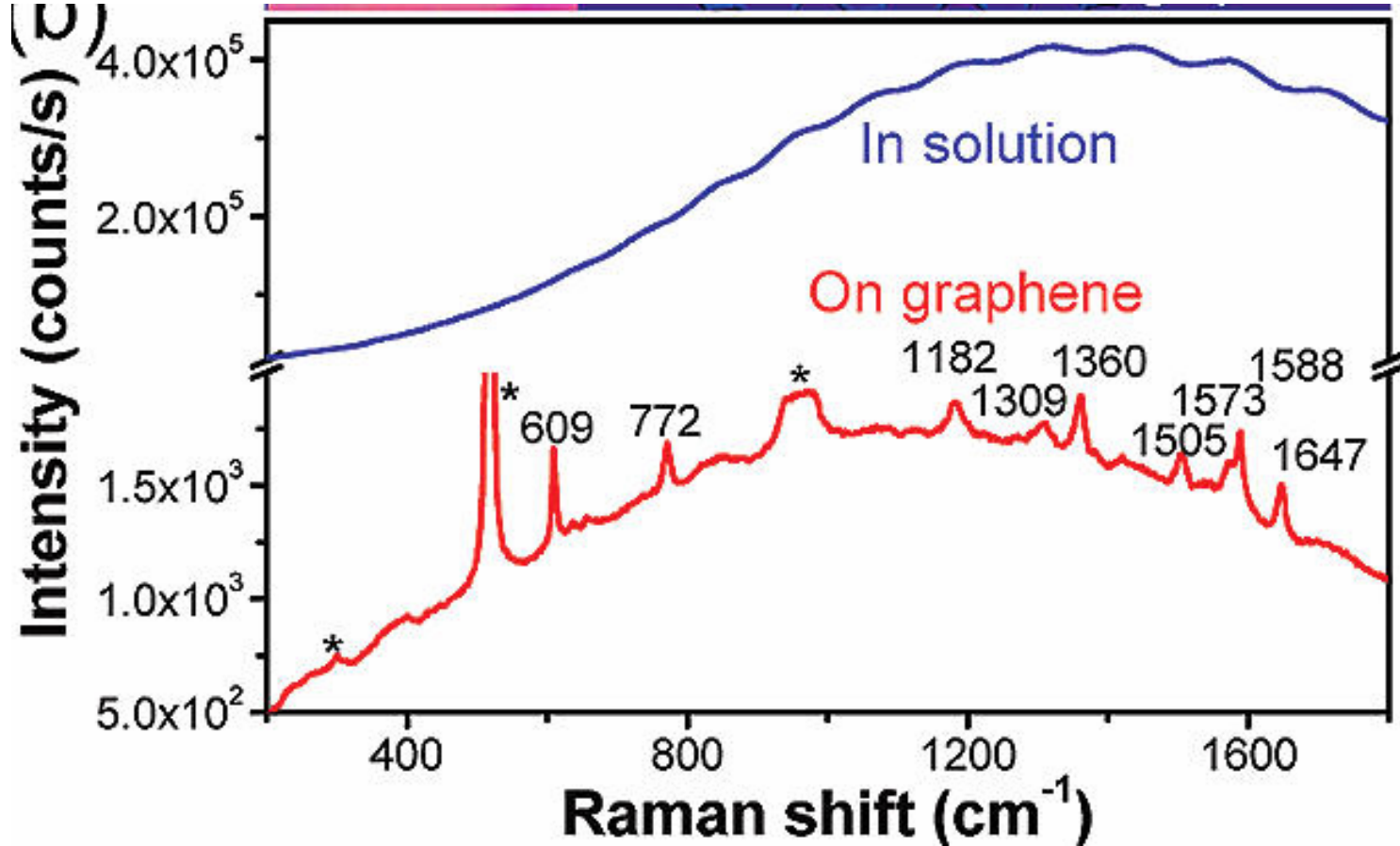
Schematic illustration of graphene as a substrate to quench FL in RRS

Experimental

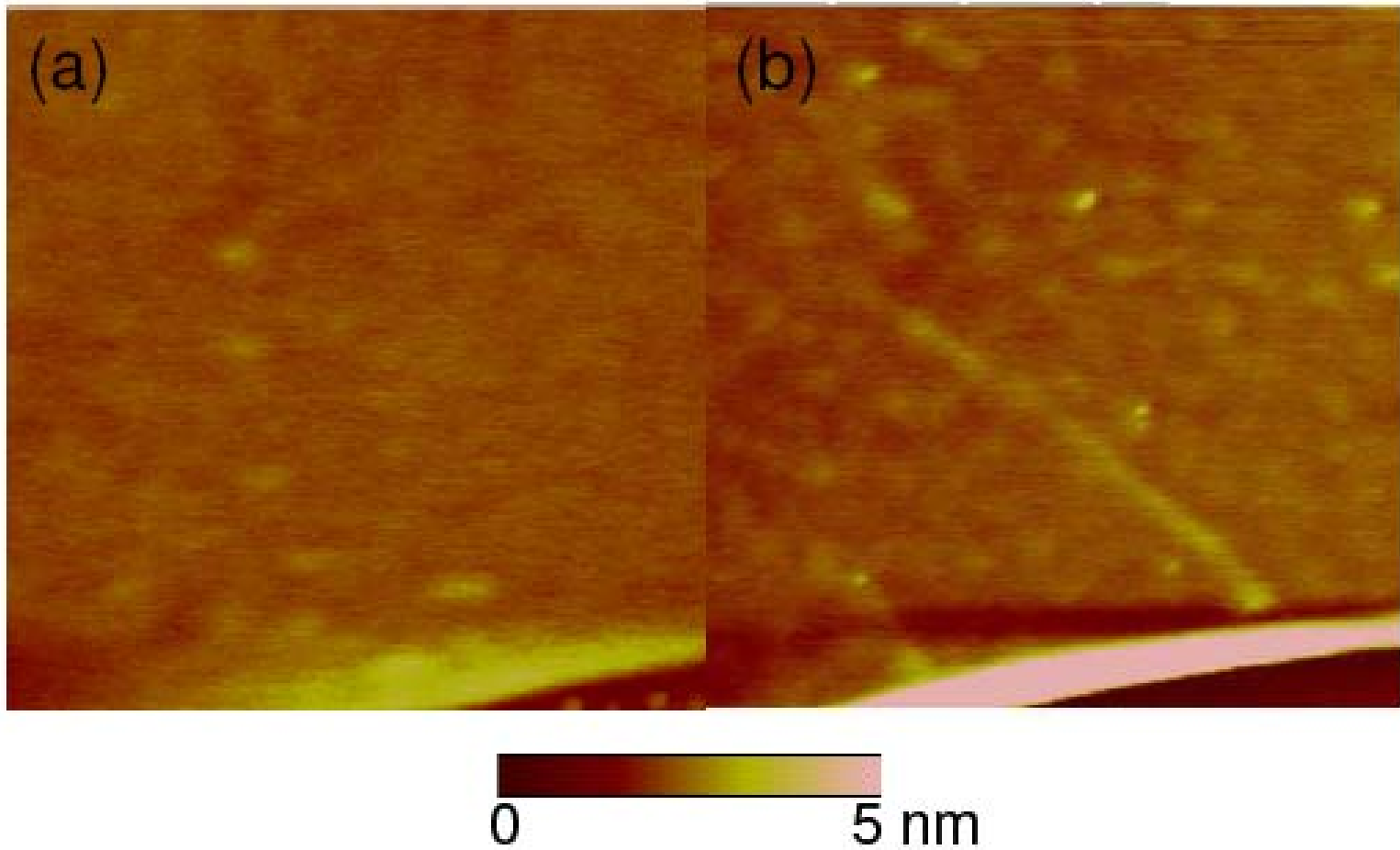
- ❖ Graphene was prepared by mechanical exfoliation of Kish graphite (Covalent Materials Corp.) on SiO₂/Si (300 nm thick oxide).
- ❖ Graphene on SiO₂/Si was soaked in R6G solution (10 μM in water) or PPP solution (20 μM in methanol) for 30 min.
- ❖ Then the graphene sample with adsorbates was rinsed in the corresponding solvent for ~15 min and then dried under a N₂ flow.
- ❖ The laser power on the sample was ~0.6 mW for 514 nm and 4 mW for 633 nm.



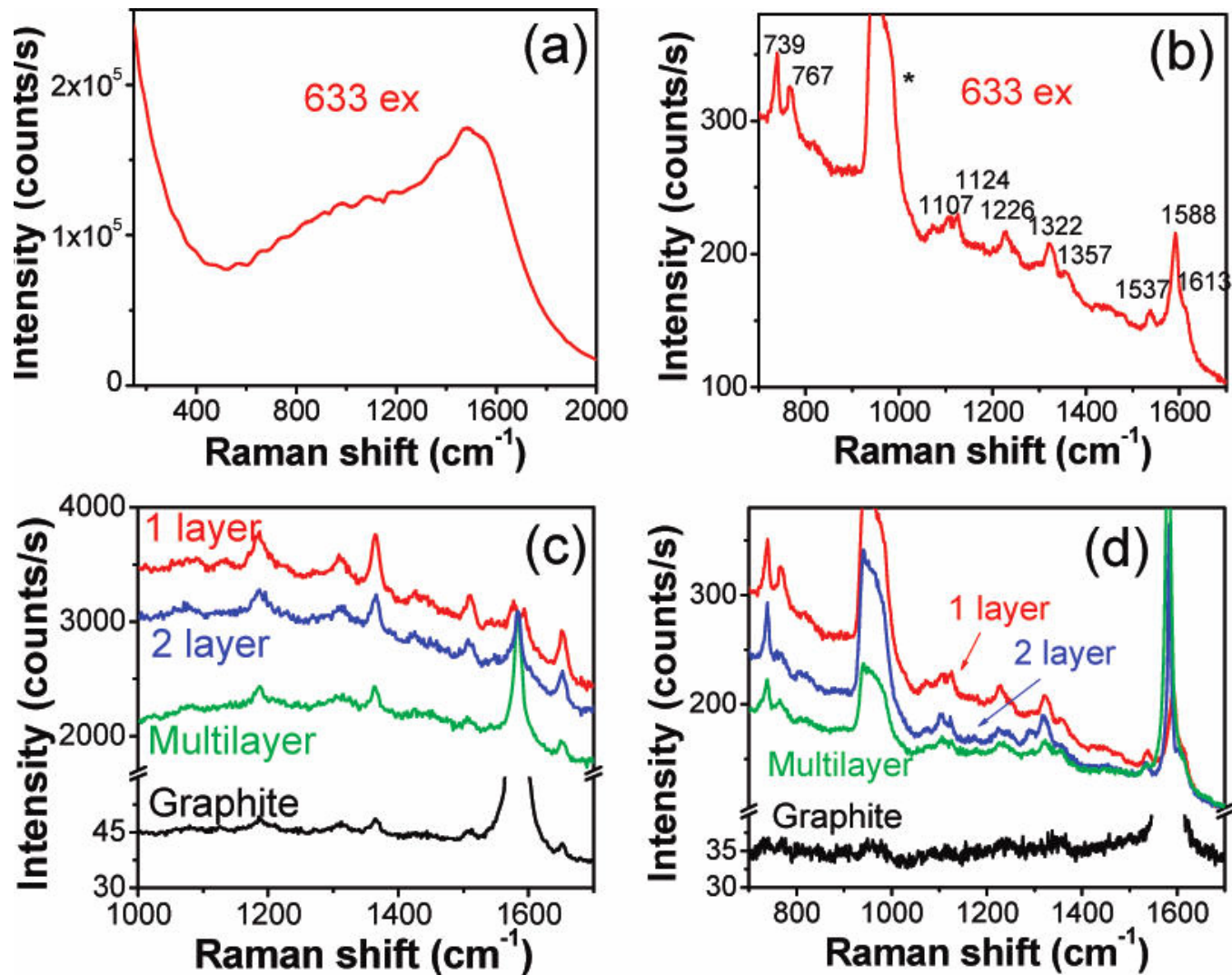
(a), (b) Optical images of graphenes with different layers and graphite pieces. (c) Raman spectra (at 633 nm excitation) from the position P1, P2, P3 and P4 in panel (a) and (b). From the optical images, P1 and P2 were identified as few layer graphenes, P3 was identified as a multilayer graphene ($10 < n < 50$) and P4 was identified as a graphite piece. Raman characterization identified P1 as a monolayer graphene and P2 as a bilayer graphene^{1, 2}. The spectra in (c) were integrated by 60s.



Raman-FL spectra of R6G in water (10 μM) (blue line) and R6G on a 1L graphene (red line) at 514 nm excitation. The Raman peaks labeled as * were from the SiO_2/Si substrate. The 1588 cm^{-1} peak was from graphene.



AFM images of a 1L graphene (a) before and (b) after R6G adsorption. All images are in sizes of $1 \times 1 \mu\text{m}^2$. The edge was curled after R6G solution treatment.



Raman-FL spectra of PPP (a) in solution and (b) on a 1L graphene at 633 nm excitation. The peak labeled as * was from SiO_2/Si . The 1588 cm^{-1} peak was from graphene. Raman-FL spectra of (c) R6G (514 nm excitation) and (d) PPP (633 nm excitation) on different surfaces.

Possible reasons for the larger Raman/FL intensity ratio

- (a) An increased RRS cross section.
- (b) Aggregation-induced FL quenching for R6G and PPP on graphene.
- (c) Photobleaching of R6G and PPP on graphene.
- (d) **Graphene-induced FL quenching.**

- The greatly increased Raman/FL intensity ratio is mainly attributed to graphene-induced FL quenching.
- A similar result has been reported for dyes on graphitic carbon.
- For R6G on graphene, FL quenching may be mainly via energy transfer because calculation has shown a fast energy transfer from dyes to graphene and energy transfer from R6G to metals has usually been observed.
- For PPP on graphene, both energy and electron transfer are possible because both energy and electron transfer have been observed in a similar system (porphyrins on CNTs).

$$q = \frac{\sigma_{\text{FL in solution}}}{\sigma_{\text{FL on graphene}}} = \frac{\sigma_{\text{FL in solution}}}{\sigma_{\text{Raman on graphene}} \frac{A_{\text{FL on graphene}}}{A_{\text{Raman on graphene}}}}$$

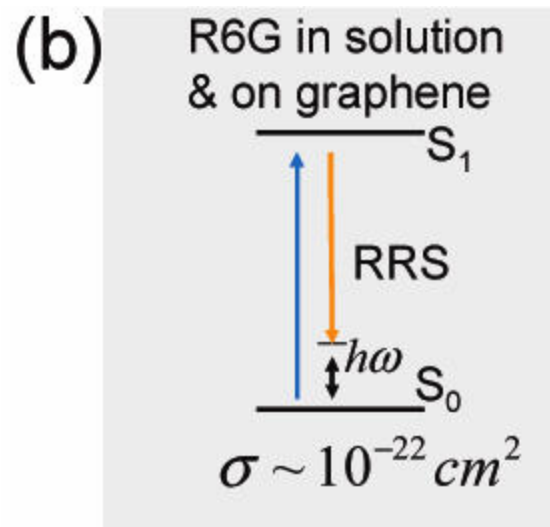
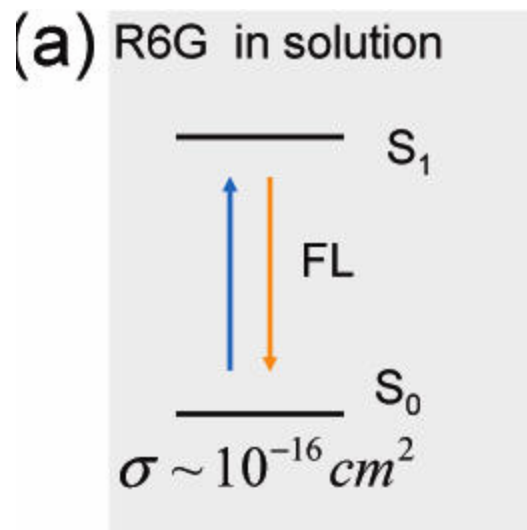
q = FL quenching

σ = cross section

A = integrated area

Graphene-induced FL quenching (q) is estimated to be $\sim 10^3$

Summary of (a) FL and (b) Raman cross section (σ) of R6G in solution and on graphene



S_0 : ground state, S_1 : excited state

Conclusion

- By adsorption of R6G and PPP on graphene, we have observed RRS peaks of R6G and PPP over their FL background.
- The successful observation of Raman peaks is mainly attributed to graphene-induced FL quenching.
- Graphene has an aromatic and hence hydrophobic and almost nonreactive surface, which offers an alternative way for RRS measurement of fluorescent molecules.

Thanks