Theoretical studies of electronic conductivity of aromatic hydrocarbons using green's function-based elastic scattering theory

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In molecular devices, delocalization of π-electrons of polycyclic aromatic hydrocarbons (PAHs), such as rubrene, polyacene and graphene, can be useful for electronic conductivity, photo-absorption, chemical sensing and so on. For example, rubrene and polyacenes have been applied to accepter of organic solar cells. In addition, π-electrons of PAHs are easily affected by chemical modification. Because conductivity was affected by modification, these phenomena would be applied to control the efficiency of solar cells, chemical sensor and so on. There were several attempts to control the electronic conductivities of PAHs. Enoki and coworkers reported that conductivity of graphene flakes was increased by exposing to oxygen gas[1]. Theoretical methods were significant to investigate mechanism these effects. According to our previous studies, however, triplet oxygen molecule ($^3O_2$) and closed shell PAHs interacted repulsively[2]. Therefore, in this study, we proposed that open shell structures in order to encourage the interactions.

First, to reveal the effects of gas molecule to π-electrons of PAHs, interactions between PAHs which had radical character and $^3O_2$ were examined with DFT calculations[3]. We employed phenalenyl radical as the models of simplest open shell PAHs. In the results, $^3O_2$ can be endothermically adsorbed onto radical site on phenalenyl radical. Second, we investigated possibility of adsorption of $^3O_2$ onto larger PAHs, such as zethrene. Zethrene and larger systems have singlet biradical character because such molecules had two units of phenalenyl like structure. Then, the larger systems adsorbed more easily $^3O_2$ than the case of phenalenyl. Variation of electronic conductivity was also calculated. In previous studies of our group, the theoretical method for electronic conductivity with Landauer formula was developed and applied to several nanoscale systems[4]. In the results, conductivity of zethrene was risen by adsorption of $^3O_2$.

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