

Click Chemistry Approach for the Covalent Modification of Graphene with Conjugated Poly(fluorene)

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Conjugated polymeric materials have been extensively investigated due to their potential commercial applications in molecular-scale electronics including light-emitting diodes, electrochromic displays, field-effect transistors, integrated circuits or solar cells [1]. In the last case the active layer of polymeric devices is a donor–acceptor bulk heterojunction composed of a conjugated donor polymer mixed with acceptor molecules or macromolecules [2].

The fascinating properties of Graphene, a one-atom-thick planar sheet of sp²-bonded carbon atoms in a quasi-2-dimensional (2D) disposition have made it one of the most promising materials of the first decade of the 21st century [3]. Its electronic properties, particularly incredible electron mobility and large specific area render it a competitive alternative as electron-accepting material in photovoltaic device applications.

In order to prepare graphene/conjugated polymers we thought click chemistry to be the ideal tool because of its modular nature, high selectivity, reactivity and reliability. Here we describe the click reaction between alkyne-functionalized graphene (alqG) and Poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis-(6-azidohexyl) fluorene)] (PFA). This is the first study of a broad work schedule planed in order to study the superior properties of graphene-reinforced composite obtained from click coupling between graphene and both conjugated and conventional polymers.

The alqG e was obtained by reduction of GO in alkaline aqueous medium followed by coupling reaction with 4-ethynylaniline at 80° C using isoamyl nitrite. The success of the reaction was confirmed by FTIR, Raman and HNMR spectroscopy. Subsequently, the click reaction was carried out by mixing the alqG with the PFA using CuBr and PMDETA as catalytic system (Figure 1). The product was named PFA-click-alqG. The success of the click reaction was supported by FTIR, where the band around 2090 cm⁻¹, assigned to the azide group, markedly diminishes. The band did not completely disappear probably because the concentration of alkynes immobilized in graphene sheets is lower than that content of azide in the PFA. More studies are being undertaken in order to obtain the optimal reaction conditions.

Interesting results were obtained when the absorption/emission spectra were collected in a range of solvents with different polarities. For instance, in o-dichlorobenzene (o-DCB) the UV-visible and fluorescence spectra of the PFA-click-alqG resemble that obtained for the pure PFA suggesting no effect of the graphene on the electronic behaviour of the polymer. However, in a more polar solvent, dimethylformamide (DMF), the maximum absorption band blue shifted around 50 nm and the emission spectra of the polymer retained only a 10% of the original photoluminescence. This quenching may be originated by resonance energy transfer from the excited state of PFA to graphene.

The above results indicate that the PFA-click-alqG adopt different structures (with some degree of ordering) depending on the surrounding environment. In the first case, o-DCB it is a good solvent for graphene, keeping it away from the PFA chains; while in DMF, a poor solvent for graphene, graphene is folded polymer favouring the energy transfer and quenching.

These are preliminary results and more experiments are being conducted to confirm the above hypothesis.

References

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Figures

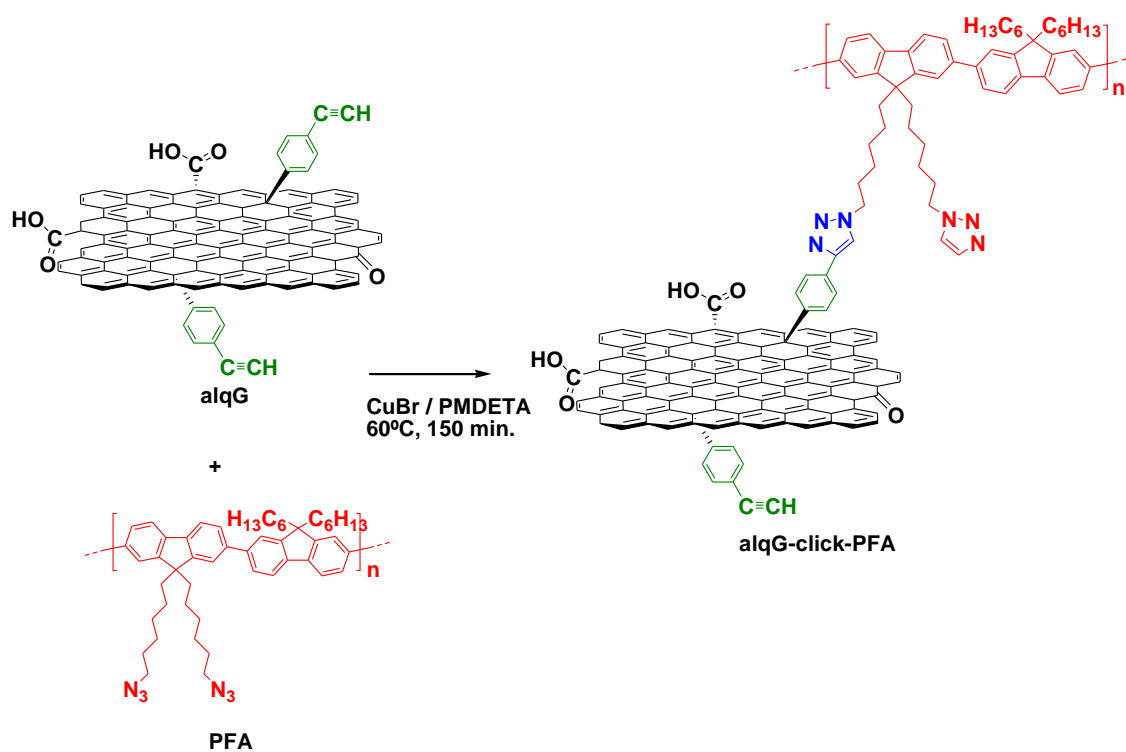


Figure 1. Draw representing the click coupling of graphene with PFA.