Revealing excited states dynamics in cross-linked covalent hybrids of graphene and diketopyrrolopyrrole oligomers via ultrafast transient absorption spectroscopy

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Abstract. We report on ultrafast dynamics in cross-linked covalent hybrids of graphene and diketopyrrolopyrrole (TDPP) oligomers. Comparisons between non-polymerizing (EXG-TDPP) and polymerizing (c-EXG-TDPP) hybrids show that charge/energy transfer occurs faster than 50 ps in EXG-TDPP, while the c-EXG-TDPP system shows quenching within 18 ps. The transient response of c-EXG-TDPP is completely quenched (~99%), while in EXG-TDPP full quenching occurs after 1.39 ns. Photocurrent studies of c-EXG-TDPP films show IPCE > 2%, indicating ultrafast charge transfer between TDPP and graphene.

1 Introduction

One promising class of synthetic systems in which efficient energy/charge transfer may be achieved is graphene-based materials (GBMs). Graphene monolayers exhibit exquisitely high carrier mobilities, broadband absorption (2.3% per monolayer), and ultrafast optical non-linearities such as saturable absorption [1].

The utility of graphene can be enhanced further via functionalization, either with nanoparticles or molecules, and via covalent or non-covalent linkages [2]. Sensitization of graphene via attachment of strongly-absorbing chromophores may provide a new avenue for the development of cheap and non-toxic solar cells. Additionally, the presence of graphene, whether via covalent or non-covalent linkage, has been shown to significantly modify the electronic properties of chromophores [3].

Here we investigate the ultrafast dynamics of mechanically-exfoliated few-layer graphene and diketopyrrolopyrrole oligomers via ultrafast transient absorption spectroscopy with 70 fs time resolution. Two hybrids are studied in comparison to the isolated Ph2TDPP chromophore, one of which (c-EXG-TDPP) cross-links graphene flakes via long polymeric backbone chains of TDPP, and the other of which (EXG-TDPP) does not polymerize (Figure 1). While quenching of the transient optical absorption is observed in both samples, the efficiency of this quenching process is shown to be much higher in c-EXG-TDPP compared to EXG-TDPP.

2 Results

We examined a recently developed cross-linked covalent hybrid between few-layer graphene flakes and bifunctional diphenyl-dithiophenediketopyrrolopyrrole (Ph2TDPP) units [3,4]; the resulting cross-linked structure is referred to as c-EXG-TDPP. A similar model hybrid unit that does not cross-link is referred to EXG-TDPP (Figure 1). These samples are dissolved in toluene and placed in 1 mm path length cuvettes. It was confirmed here via steady-state linear absorption and emission experiments that the electronic properties of the cross-linked system c-EXG-TDPP are modified significantly compared to both Ph2TDPP and EXG-TDPP: the main absorption band of Ph2TDPP is red-shifted by 66 nm in c-EXG-TDPP, indicating a large increase in conjugation length along the polymeric backbone chain. These changes in electronic properties may explain the differences in charge/energy transfer processes between the two hybrids.

The ultrafast dynamics of both the base unit Ph2TDPP, and the two hybrids, are studied via ultrafast transient absorption spectroscopy. A non-collinear optical parametric amplifier (NOPA) is pumped with 800 nm,
Also observed in linear absorption, features of absorption signal is quenched within 18 ps time, indicating an in-filling of the excited singlet states from higher-lying states. The full transient absorption signal is quenched within 18 ps. Since the GSB features observed from 600-660 nm in the 18 ps DAS are similar to those associated with the excited singlet states of Ph$_2$TDPP, we believe preliminarily that charge separation between the TDPP moieties and covalently-bound graphene occurs on the 18 ps timescale, and that the charge separated state may not be optically active. This phenomenon may be explained by the increased conjugation length in c-EXG-TDPP, which could lead to a more stable charge separated state than in EXG-TDPP. It is also expected that there is an interplay between charge transfer from nearest TDPP moieties attached directly to graphene, energy transfer to graphene from more distant TDPP moieties, and increased conjugation length in c-EXG-TDPP compared to oligomeric EXG-TDPP.

Photocurrent measurements of c-EXG-TDPP films indicate that a charge transfer process is taking place, with incident photon to electron conversion efficiencies (IPCE) > 2%. This result may confirm the rapid charge separation process occurring in c-EXG-TDPP; photocurrent collection is further enhanced likely due to transport of the extracted electron along the graphene scaffolding. Photocurrents were not detected for Ph$_2$TDPP or non-film-forming EXG-TDPP drop-cast samples. We conclude that energy/charge transfer processes in these hybrid graphene-dye systems that occur on sub 50 ps timescales are observed using ultrafast transient absorption spectroscopy, with charge transfer confirmed by photocurrent measurements.

References