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Original
Revealing excited states dynamics in cross-linked covalent hybrids of graphene and diketopyrrolopyrrole oligomers via ultrafast transient absorption spectroscopy / Ross, A.M., Zheng, M., Maggini, M., Marangi, F., Cerullo, G., Gatti, T., Scotognella, F.. - In: EPJ WEB OF CONFERENCES. - ISSN 2100-014X. - 238:(2020), p. 07007. (EOS Annual Meeting (EOSAM 2020)) [10.1051/epjconf/202023807007].

Availability:
This version is available at: 11583/2977574 since: 2023-03-29T11:13:16Z

Publisher:
EDP Sciences

Published
DOI:10.1051/epjconf/202023807007

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12 September 2026

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 Ph_2TDPP 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-dithiophenedikethopyrrolopyrrole (Ph_2TDPP) units [3,4]; the resulting cross-linked structure

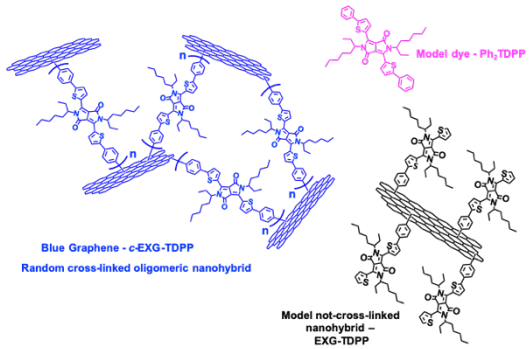

Figure 1: Structure of the cross-linked graphene-dithiophenediketopyrrolopyrrole hybrid c-EXG-TDPP, of the model Ph_2TDPP chromophore unit constituting its cross-linking oligomers, and of the analogous hybrid system lacking cross-linking EXG-TDPP.

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 Ph_2TDPP and EXG-TDPP: the main absorption band of Ph_2TDPP 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 Ph_2TDPP, and the two hybrids, are studied via ultrafast transient absorption spectroscopy. A non-collinear optical parametric amplifier (NOPA) is pumped with 800 nm,

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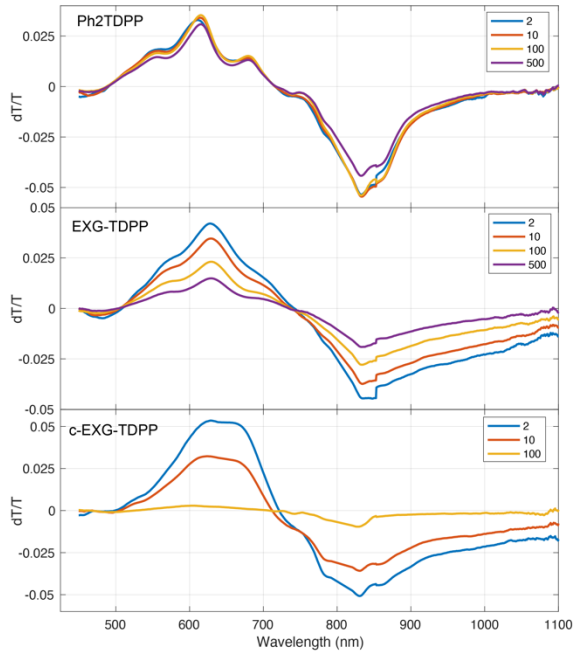

Figure 2: Transient absorption spectra for Ph_2TDPP, EXG-TDPP, and c-EXG-TDPP at selected pump-probe delay times (labeled in picoseconds in legend). Discontinuity at ~850 nm is due to stitching between different experimental runs.

150 fs pulses generated by a chirped pulse amplified (CPA) Ti:sapphire laser at a 1 kHz repetition rate, yielding sub-100 fs pulses at 575, 625, and 645 nm [5], used to pump Ph_2TDPP, EXG-TDPP, and c-EXG-TDPP, respectively. Broadband white light is generated in a sapphire crystal as a probe, and differential transmission ($\Delta T/T$) is measured by comparing the transmission of the probe through the sample when the pump is blocked/unblocked.

Global analysis of $\Delta T/T$ spectra (Fig. 2) using the sum of three exponentials allowed for the elucidation of energy/charge transfer processes. In EXG-TDPP, a process faster than 50 ps is observed, followed by a much longer decay with a lifetime of 1.39 ns, in agreement with previous TRPL measurements [3]. Ground state bleaching (GSB) features are observed at 575 and 645 nm, stimulated emission (SE) signals are observed at 700 nm; these results are in agreement with linear absorption and steady-state emission. A broad excited-state absorption (ESA) band is observed starting at 725 nm, and extending out into the NIR past 950 nm. The decay-associated spectrum (DAS) extracted via global fitting (not shown) associated with the 47 ps lifetime is broadened out into the NIR farther than both Ph_2TDPP ESA features and the longer EXG-TDPP DAS with lifetime of 1.39 ns; this may indicate the presence of a charge-transfer state, which is followed by back electron transfer into the TDPP moiety.

However, much more efficient and rapid quenching is observed in c-EXG-TDPP: a broad DAS with lifetime 3.8 ps is observed at longer wavelengths than the main GSB peaks, 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 also observed in linear absorption, and the ESA features are similar to those associated with the excited singlet states of Ph_2TDPP, 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_2TDPP 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.

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