



## Functionalized fluorographenes with important non linear optical properties

I. Papadakis<sup>1,2#,\*</sup>, A. Stathis<sup>1,2</sup>, N. Karampitsos<sup>1,2</sup>, M. Stavrou<sup>1,2</sup>, D. Kyrginas<sup>1,2</sup> and S. Couris<sup>1,2</sup>

<sup>1</sup> Department of Physics, University of Patras, 26504 Rio, Patras, Greece

<sup>2</sup> Institute of Chemical Engineering Sciences (ICE-HT), Foundation for Research and Technology, Hellas (FORTH), Patras, 26504 Patras, Greece#

Presenting author: I. Papadakis, email: [i.papadakis@iceht.forth.gr](mailto:i.papadakis@iceht.forth.gr)

\* Corresponding author: I. Papadakis, email: [i.papadakis@iceht.forth.gr](mailto:i.papadakis@iceht.forth.gr)

### ABSTRACT

In this work, the non linear optical (NLO) properties of some fluorographene derivatives are presented and compared to that of pristine fluorographene. For the investigation of the NLO response (i.e., the NLO absorption and refraction) of the fluorographene derivatives the Z-scan technique<sup>[1]</sup> was used employing 35 ps laser pulses at 532 nm and 1064 nm.

The derivatives, namely, methoxy-thiophenol- (or CF-MTP)<sup>[2]</sup>, dimethyl-amino-thiophenol- (or CF-DMATP)<sup>[2]</sup> and diethylamino-modified fluorographene (or CDEA)<sup>[3]</sup> were obtained by the reaction of fluorographene (CF) with the corresponding thiols for the case of CF-MTP and CF-DMATP and lithium diethylamide for the case of CDEA. Partial nucleophilic substitution/reduction of the substrate results in sp<sup>3</sup> carbons bonded to thiol/diethylamine groups or fluorine atoms and in distinct sp<sup>2</sup> graphenic domains. The thiol/diethylamine groups act as strong electron donors, the C-F groups as strong electron acceptors and the sp<sup>2</sup> domains as π-conjugated bridges, thus representing a classical donor-π bridge-acceptor NLO chromophore.

All fluorographene derivatives exhibited strong Saturable Absorption (SA, i.e.,  $\text{Im}\chi^{(3)} < 0$ ) under visible and infrared ps excitation, whereas the parent fluorographene exhibited negligible NLO absorption. Furthermore, the stoichiometry of the derivatives, as well as the degree of functionalization, affected greatly the NLO refractive part of  $\chi^{(3)}$ , while again the parent fluorographene exhibited negligible NLO refraction.

As a general conclusion, the diethylamino-fluorographene, CDEA, was found exhibiting systematically over an order of magnitude higher third-order nonlinear susceptibility  $\chi^{(3)}$  than the dimethyl-amino-thiophenol-fluorographene, CF-DMATP and two orders of magnitude higher than the methoxy-thiophenol-fluorographene, CF-MTP. The diethylamino- groups are amongst the strongest electron donors and thus, the enhanced NLO response is attributed to more efficient charge transferring based on the classical charge-transfer chromophore mentioned above. More importantly, all derivatives exhibited important NLO properties whereas the parent fluorographene exhibited negligible response under both visible and infrared 35 ps laser excitation. This suggests an ON/OFF switching of the NLO response attributed solely to the different functionalization of the samples. As such, this work shows how functionalization can provide simple tools for customizing the NLO response and properties of fluorographene derivatives, making them suitable for various applications.

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### REFERENCES

- [1] Couris S., Koudoumas E., Ruth A. A. and Leach S. 1996 *J. Phys. B: At. Mol. Opt. Phys.*, **28**, 4537-4554.
- [2] Stathis A., Papadakis I., Karampitsos N., Couris S., Potsi G., Bourlinos A., Otyepka M. and Zboril R. 2019 *ChemPlusChem*, **84**, 1-12.
- [3] Papadakis I., Kyrginas D., Stathis A., Couris S., Potsi G., Bourlinos A., Tomanec O., Otyepka M. and Zboril R. 2019 *J. Phys. Chem. C*, under review.