## CHEM2DMAC

## Covalent surface functionalization of graphene based materials controlled by blue light

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We present an unprecedented methodology for the covalent functionalization [1] (arylation) of different sp<sup>2</sup> carbon-based materials with arylazo sulfones: i) Chemical Vapor Deposited Graphene on Cu (CVD-G), ii) Graphene Oxide, iii) reduced Graphene Oxide (rGO), iv) considering also the highly oriented pyrolytic graphite (HOPG) as ideal 100% sp<sup>2</sup> substrate.

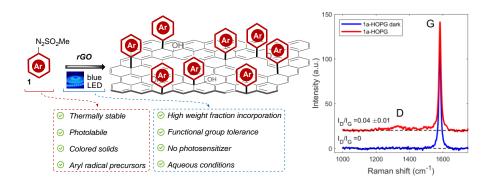
The reaction can be activated by commercial blue led (461 nm). Mild reaction conditions, absence of photosensitizers, functional group tolerance and high atomic fractions (XPS analysis) represent some of the salient features characterizing the present methodology. The study was completed by a mechanistic proposal based on both experimental as well as spectroscopic analyses, in particular n Raman analysis on HOPG [2] and CVD-G, where D peak was observed after functionalization. The quantitative analytical determination of the tagged aryl units via XPS, represent a unique combination of factors electing the present methodology as a valuable synthetic alternative to the known protocols based on electrochemical charge transfer [3,4] for the covalent modification of a wide range of graphene based materials.

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## References

- [1] Sauer, Y. Liu, A. De Nisi, S. Protti, M. Fagnogni, M. Bandini, ChemCatChem 2017, 9, 4456-4459
- [2] Lombardi L., Kovtun A., Mantovani S., Bertuzzi G., Favaretto L., Bettini C., Palermo V., Melucci M., Bandini M. Chemistry—A European Journal 2022, e202200333
- [3] Sinitsikii, A.; Dimiev, A.; Corley, D. A.; Fursina, A. A.; Kosynkin, D. V.; Tour, J. M. ACS Nano 2010, 4, 1949
- [4] Greenwood, J.; Phan, T. H.; Fujita, Y.; Li, Z.; Ivasenko, O.; Vanderlinden, W.; Van Group, H.; Frederick, W.; Lu, G.; Tahara, K.; Tobe, Y.; Uji-I, H.; Mertens, S. F. L.; De Feyter, S., ACS Nano 2015, 9, 5520

## **Figures**



**Figure 1:** left: schematic representation of the present visible-light assisted covalent arylation of rGO with arylazo sulfones. Right: Raman spectrum of 1a-HOPG dark and 1a-HOPG. Linear background was subtracted, and spectra were shifted for clarity.