



# More is not always better: Dissociative photoionization limits the EUV absorbing photoacid generator pentafluorophenyl triflate in photolithography

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High EUV absorption is often considered a key design criterion for next-generation photoacid generators (PAGs) in chemically-amplified EUV photoresists, but absorption alone does not guarantee productive acid formation. This is exemplified by pentafluorophenyl triflate, a highly fluorinated and thus absorbing, neutral PAG candidate proposed for chemically amplified resists in extreme ultraviolet (EUV) lithography. In this work, we show that its strong EUV absorption is outweighed by unfavorable dissociative photoionization pathways at the 92 eV photon energy used in EUV scanners. By combining photoelectron-photoion coincidence (PEPICO) spectroscopy with quantum-chemical calculations, we resolve the fragmentation chemistry of pentafluorophenyl triflate and identify the dominant channels that compete with photoacid generation. The photoionization mass spectrum is dominated by fragmentation: the intact parent ion contributes only approximately 3% of the total signal, while  $\text{CF}_3^+$  is the major product ion. Calculated appearance energies reproduce the experimental trends and support a sequential decomposition mechanism involving loss of  $\text{SO}_2$ ,  $\text{CF}_3$ , and  $\text{CO}$ . Crucially, the main dissociation pathways do not generate fragments that can serve as precursors to triflic acid, the strong acid required to drive deprotection in chemically amplified resists. Together with earlier dissociative electron attachment results,<sup>[1]</sup> these findings reveal why pentafluorophenyl triflate fails as an effective EUV PAG despite its high absorption cross section. More broadly, this study demonstrates that molecular design for EUV lithography must move beyond absorption maximization and explicitly account for the elementary ionization, fragmentation, and electron-induced processes that determine chemical functionality under EUV exposure.

## References

[1] M. Mendes, R. Tafrishi, P. Guerra, F. Holzmeier, O. Ingólfsson, F. Ferreira da Silva, *iScience* 2025, **28**, 114020.