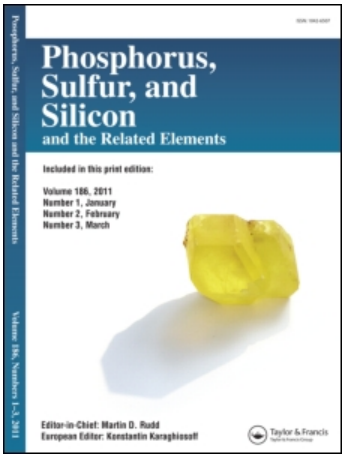

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Role of Alkylthio Substituents on Tetrathiafulvalene and 1,3-Dithiole Rings: A Theoretical Study

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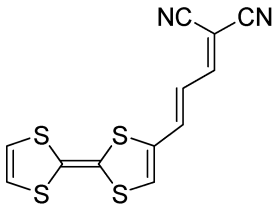
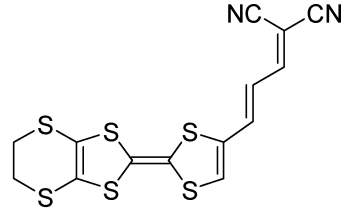
The effect of alkylthio substituents on the redox and nonlinear optical behavior of tetrathiafulvalenes has been studied by Density Functional Theory Calculations.

Keywords Density Functional Theory; nonlinear optics; tetrathiafulvalene

Alkylthio substituents commonly considered as donor groups cause increased oxidation potentials when attached to tetrathiafulvalenes and are consequently regarded as electron-withdrawing groups relative to this strong donor. However, the recent discovery of tetrathiafulvalene-derived donor–acceptor molecules with second order nonlinear optical activity[1] questions that assumption because the introduction of alkylthio groups renders tetrathiafulvalene a better donor and increases the nonlinear optical activity of these molecules.



E_1= 0.54V; E_2= 0.84V
$\mu\beta(0)$ = 470 10^{-48} esu
λ_{max} = 633 nm



E_1= 0.59V; E_2= 0.90V
$\mu\beta(0)$ = 560 10^{-48} esu
λ_{max} = 612 nm

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To clarify the effect of alkylthio groups on these processes, we have performed DFT calculations. The results obtained reveal that alkylthio groups behave as weak electron donors and the unexpectedly high oxidation potentials are mainly due to solvent effects. Furthermore, PCM-DFT calculations provide an accurate prediction of the oxidation potential of alkylthio-substituted tetrathiafulvalenes. On the other hand, solvent effects in 1,4-bis(alkylthio)-1,3-dithole-2-ones are not large enough to overcome the electron-donor character of alkylthio groups and these compounds are calculated to have lower oxidation potentials than the unsubstituted 1,3-dithiol-2-thione.

Concerning the nonlinear optical behavior, the lowest energy absorption is mainly contributed from the HOMO → LUMO transition, but there are also contributions from HOMO-1 → LUMO and HOMO-2 → LUMO. Charge transfer from the substituents to the LUMO is explained by the large participation of substituent sulfur atoms to HOMO-1 and HOMO-2 and gives rise to increased excited state dipole moments and larger hyperpolarizabilites compared to unsubstituted TTF-derived NLO-phores.

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