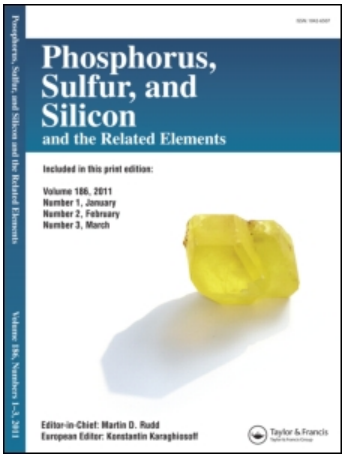

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1,3-Dithiole Based Quinoid Systems: Multiply Proaromatic NLO-Phores

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1,3-Dithiole Based Quinoid Systems: Multiply Proaromatic NLO-Phores

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INTRODUCTION

Dipolar donor-π-acceptor (D-π-A) compounds have been widely studied in the search for high second-order nonlinear optical (NLO) responses. To that end, most of the structures studied so far make use of aromatic donors, such as anilino or ferrocene derivatives and polyenic spacers. On the other hand, systems comprising proaromatic moieties have been much less studied.

RESULTS AND DISCUSION

In this communication, and as a continuation of our efforts to study the effect that the gain in aromaticity has on the NLO properties of merocyanines,[1] we describe the synthesis and study of structures **1** and **2**, where a quinoid spacer links a 1,3-dithiole donor fragment and an electron acceptor.

The NLO response of these compounds is strongly dependent on different factors, such as the nature of the acceptor group, the length of the spacer, and the proaromaticity of the latter, which can be modulated through benzoannelation. Thus, progressive benzoannelation of

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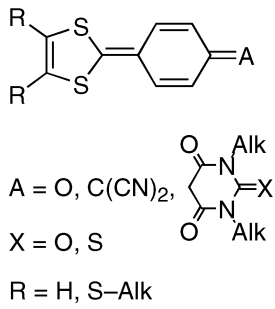
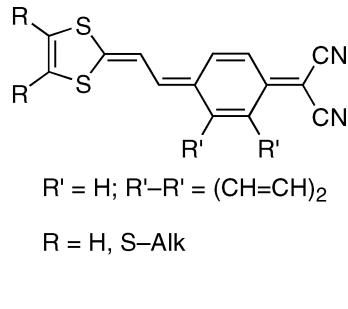


(**1**)



(**2**)

the spacer results in structures with more quinoid character and, therefore, with more positive $\mu\beta$ values.

Somewhat unexpectedly, the contribution of the neutral and zwitterionic limiting forms to the description of these molecules is also dependent on the presence of *S*-substituents on the dithiole ring, which cause an increase in the zwitterionic character of the excited state, giving rise to more positive $\mu\beta$ values than those of the corresponding unsubstituted (R = H) derivatives.

Ab initio and DFT calculations support the experimental measurements (EFISH technique) carried out on these doubly (and triply) proaromatic NLO-phores. $\mu\beta$ values range from -2000×10^{-48} esu to $+3100 \times 10^{-48}$ esu.

REFERENCE

[1] R. Andreu, J. Garín, J. Orduna, R. Alcalá, and B. Villacampa, *Org. Lett.*, **5,** 3143 (2003).