

Synthesis and Evaluation of Thermal, Electrochemical and Nonlinear Optical Properties of Dicyano- and Tricyanovinyl-bithienylpyrroles

A. Maurício C. Fonseca,^a M. Cidália R. Castro,^a M. Belsley^b and M. Manuela M. Raposo^a

^aCenter of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

^bCenter of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

e-mail: amcf@quimica.uminho

Materials exhibiting large optical nonlinearities continue to be the subject of intense studies because of their potential applications in modern communication technologies involving optical data processing, transmission, or storage, where they are gradually replacing classical electronic devices.^[1]

Earlier we reported on the synthesis and evaluation of thermal, redox and NLO properties of donor-acceptor substituted thienylpyrrole derivatives. Our studies have shown that replacing the benzene ring of a chromophore bridge with heterocycles (thiophene, pyrrole, (benzo)thiazole), results in an enhanced molecular hyperpolarizability of conjugated donor-acceptor compounds.^[2,3,4,5,6]

As part of an on-going program to develop strong charge transfer donor-acceptor pyrrole systems with enhanced nonlinear optical (NLO) properties we have explored the potential of bithienyl-pyrrole derivatives **1-4** as efficient π -conjugated systems functionalized with dicyanovinyl- or tricyanovinyl- acceptor groups substituted at thiophene or pyrrole rings. Compounds **3a-b** were prepared, in good yields, through Knoevenagel condensation of the precursor aldehydes **2a-b** with malononitrile, and the tricyano derivative **4** were synthesized through direct tricyanovinylation reaction of **1** with tetracyanoethylene. On the other hand, bithienyl-pyrroles **1** and **2b** were prepared through palladium-catalyzed decarboxylative cross-coupling reaction between 1-methyl-1*H*-pyrrole-2-carboxylic acid and the appropriate bithienyl bromides, whereas formyl-precursor **2a** were prepared through Vilsmeier-Haack formylation from the corresponding bithienyl-pyrrole **1**.

The molecular structure, especially the degree of planarity and the relative orientations of the auxiliary donor and acceptor entities, is found to strongly influence their electrochemical and optical (linear and nonlinear) properties. Here we report on the synthesis of compounds **1-4** and evaluate their potential as efficient and thermally stable NLO materials by experimentally characterizing their redox properties, thermal stability (TGA) and second order nonlinear optical response (β_{HRS}). These results indicate that these compounds have good potential for a variety of NLO applications.

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[1] G.S. He, L.-S. Tan, Q. Zheng, P. N. Prasad *Chem. Rev.* **2008**, 108, 1245-1330.

[2] M. M. M. Raposo, A. M. R. C. Sousa, G. Kirsch, F. Ferreira, M. Belsley, E. Matos Gomes, A. M. C. Fonseca *Tetrahedron* **2005**, 61, 11991-11998.

[3] M. M. M. Raposo, A. M. R. C. Sousa, G. Kirsch, P. Cardoso, M. Belsley, E. Matos Gomes, A. M. C. Fonseca *Org. Lett.* **2006**, 8, 3681-3684.

[4] R. M. F. Batista, S. P. G. Costa, E. L. Malheiro, M. Belsley, M. M. M. Raposo *Tetrahedron* **2007**, 63, 4258-4265.

[5] M. M. M. Raposo, M. C. R. Castro, P. Schellenberg, A. M. C. Fonseca, M. Belsley *Tetrahedron* **2011**, 67, 5189-5198.

[6] M. M. M. Raposo, A. M. C. Fonseca, M. C. R. Castro, M. Belsley, M. F. S. Cardoso, L. M. Carvalho, P. J. Coelho *Dyes Pigments* **2011**, 91, 62-73.